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CHEMISTRY FOR PHOTOGRAPHERS.

BY

CHAS. F. TOWNSEND, F.C.S., F.R.P.S.

ILLUSTRATED.

THIRD EDITION, REVISED.

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CHEMISTRY FOR PHOTOGRAPHERS.

CHAPTER I.

INTRODUCTORY.

THE first essentials to anyone studying chemistry are accuracy and cleanliness. Most of the surprising results obtained by students in their early days are due to want of cleanliness. Another point I should like to impress upon those just taking up the subject is that learning "facts" in a more or less mechanical way is not learning chemistry. It is said that a good lawyer does not know much law, but knows where to find his law. The same applies to a good chemist. Above all, endeavour to get an insight into the nature of things, and remember that the proper place for a dictionary is not inside a man's head, but on a shelf. If particular sets of facts or figures are often required for reference, don't try to learn them, but cut or copy them out, give them a coat of varnish and paste them on the

The construction of a burette will readily be seen from the figure (fig. 1). The instrument can be purchased with a glass tap, or with a glass jet, a piece of india-rubber tubing and a pinchcock, the latter being quite as convenient and much cheaper. For photographic purposes, burettes for the different developing solutions should be suspended round the sink as shown in the sketch (fig. 2), being fed from stock bottles on a shelf above, when large quantities of material are used. It is well to have an opal glass plate at the back of the fixed burette, and to read the level of the bottom of the black curve at the top of the liquid when measuring. A float with a line engraved on it is sometimes used for reading, and has the advantage of keeping the solution from the air as well as or better than a stopper. The construction of a pipette will be seen from the last part of figure 1. It is filled by drawing up the liquid with the mouth: the finger is then placed rapidly on the top, and the liquid is allowed to run down to the mark. The pipette with its contents is then transferred bodily to the vessel into which it is required to run the liquid.

In the metric system, the centimetre is the measure of length, the cubic centimetre the measure of capacity, and the weight of 1 cubic centimetre of water at 15° C., or the gram, is the measure of weight. How delightfully simple these are, compared to the complicated and heterogeneous measures of the pharmacist! An inch is about 2½ centi-

metres, and an ounce about 28 grams, a fluid ounce being 28 cubic centimetres. For larger measures the litre containing 1000 c.c., and the kilogramme or kilo. of 1000 grams, are used. For small measures the decimals of the gram and the centimetre are employed. Going up the scale, 10, 100, 1000, etc., grams and centimetres follow in order, and going down the scale, $\frac{1}{10}$, $\frac{1}{100}$, $\frac{1}{1000}$ of a gram or centimetre follow one another, the decimal system being employed throughout. It is convenient to remember that a litre is very nearly a pint and three-quarters. The following table gives the means of converting English into metric equivalents, and *vice versa*.

TABLE I.—WEIGHTS AND MEASURES IN BRITISH AND METRIC SYSTEMS.

APOTHECARIES' WEIGHT (BY WHICH FORMULÆ ARE MADE UP).

20 grains=1 scruple	.	.	.	=	1.296 grams.
8 scruples=1 drachm=60 grains	=	3.887	„		
8 drachms=1 ounce=480	„	=	31.1	„	
12 ounces=1 pound=5760	„	=	373.2	„	

AVOIRDUPOIS WEIGHT (BY WHICH CHEMICALS ARE SOLD).

437½ grains=1 ounce	.	.	.	=	28.4 grams.
16 ounces=1 pound=7000 grains	=	453.59	„		

METRIC SYSTEM—WEIGHT.

10 milligrams=1 centigram	.	.	.	=	.1543 grain.	
10 centigrams=1 decigram	=	100 milligrams	=	1.543	„	
10 decigrams=1 gram	=	100 centigrams	=	15.432	„	
10 grams=1 decagram	.	.	.	=	154.323	„
10 decagrams=1 hectogram	=	100 grams	=	8 oza. 227½	grains.	
10 hectograms=1 kilogram	=	1000 grams	=	35 oza. 87½	„	

MEASURES OF LENGTH.

BRITISH.

3 barley-corns	= 1 inch	. . .	= 2.54 cm.
12 inches	. = 1 foot	. . .	= 30.48 "
3 feet	. = 1 yard	= 36 inches	= 91.44 "

METRIC.

10 millimetres	= 1 centimetre	= .3937 inch or $\frac{1}{25}$ approx.
10 centimetres	= 1 decimetre	= 3.937 "
10 decimetres	= 1 metre	= 39.37 "

FLUID MEASURE.

60 minims	= 1 drachm	. . .	= 3.5 cubic centimetres.
8 drachms	= 1 ounce	= 480 minims	= 28.4 " "
12 ounces	= 1 pound	= 5760 "	= 340.8 " "
20 ounces	= 1 pint*	. . .	= 568.0 " "
2 pints	= 1 quart	= 40 ounces	= 1.186 litres.
4 quarts	= 1 gallon	= 160 "	= 4.544 "

METRIC SYSTEM—FLUID.

1 cubic centimetre (c.c.)	. . .	= 17 minims.
10 " "	= 1 centilitre	. . . = 170 "
10 " centilitres	= 1 decilitre	= 100 c.c. = 3.52 fl. oz.
10 " decilitres	= 1 litre	= 1000 c.c. = 35.2 "

* The American pint is 16 ounces.

Many photographers have realised the convenience of a rational system, and in addition to discarding the aboriginal system of weights and measures, have adopted ten per cent. solutions for all their work. From these any developer or other dilute solution can be made up in a minimum of time. In cases of stock solutions and one or two other instances it is convenient to have a fifty per cent. solution, and in other cases five per cent., or perhaps one per cent., solutions must be employed, owing to the difficulty of dissolving a par-

ticular substance, but solutions should always be made up to contain so many parts per cent.

Some confusion in the reader's mind may be saved by pointing out again that a cubic centimetre of water weighs one gram, and a ten per cent. solution is understood to mean ten grams of the substance in one hundred of water, or one hundred grams in a litre, *i.e.*, ten grams dissolved in part of the water, and the whole made up to an even hundred, not to a hundred and ten.

Temperature is measured in this country by Fahrenheit's scale, on which the freezing point of water is 32° , and the boiling point 212° , zero being 32° below freezing point. In the Centigrade or Celsius scale employed in scientific work, and in general practice in some parts of the Continent, the freezing point of water is zero and the boiling point 100° . Table II. enables you to convert one scale into the other.

The only mathematical signs used in the explanations will be

+ added to
 - subtracted from
 $\times$ multiplied by
 $\div$ divided by
 = equals

and the signs for a proportion, namely,

As is to so is to the figure required,

2 : 4 :: 3 : x

that is to say,

$$4 \times 3 \div 2 = 6.$$

TABLE II.—THERMOMETERS. COMPARISON OF
FAHRENHEIT AND CENTIGRADE (CELSIUS) SCALES.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
100 B.	212 B.	65	149	30	86
99	210·2	64	147·2	29	84·2
98	208·4	63	145·4	28	82·4
97	206·6	62	143·6	27	80·6
96	204·8	61	141·8	26	78·8
95	203	60	140	25	77
94	201·2	59	138·2	24	75·2
93	199·4	58	136·4	23	73·4
92	197·6	57	134·6	22	71·6
91	195·8	56	132·8	21	69·8
90	194	55	131	20	68
89	192·2	54	129·2	19	66·2
88	190·4	53	127·4	18	64·4
87	188·6	52	125·6	17	62·6
86	186·8	51	123·8	16	60·8
85	185	50	122	15	59
84	183·2	49	120·2	14	57·2
83	181·4	48	118·4	13	55·4
82	179·6	47	116·6	12	53·6
81	177·8	46	114·8	11	51·8
80	176	45	113	10	50
79	174·2	44	111·2	9	48·2
78	172·4	43	109·4	8	46·4
77	170·6	42	107·6	7	44·6
76	168·8	41	105·8	6	42·8
75	167	40	104	5	41
74	165·2	39	102·2	4	39·2
73	163·4	38	100·4	3	37·4
72	161·6	37	98·6	2	35·6
71	159·8	36	96·8	1	33·8
70	158	35	95	Zero	32
69	156·2	34	93·2		
68	154·4	33	91·4		
67	152·6	32	89·6		
66	150·8	31	87·8		

CHAPTER II.

CHEMISTRY GENERALLY, AND THE CHEMISTRY OF THE
SILVER SALTS IN PARTICULAR.

AT the beginning of the book mention was made of the importance of cleanliness. "Dirt" in a chemical sense is much more comprehensive than is usually understood. To get any vessel chemically clean is not an easy process, and a vessel, after containing most chemicals, requires several careful washings before it is fit for use again. The difficulty about chemical dirt is that it is not always visible to the eye. The porcelain dish used to contain the "hypo." bath may look beautifully clean after it has been washed out, yet the porcelain is probably saturated with "hypo.," which will dissolve into the next solution placed in the dish, if used for anything but "hypo.," and spoil all the plates and paper it comes into contact with. Three careful washings are generally sufficient to cleanse an article thoroughly, but in cases where very careful cleansing is required, such as plates used for coating in the wet plate process, a powerful mixture, such as the following, must be employed, which burns up

any dirt. Never allow the mixture to get on to clothes or fingers!

Potassium bichromate,	. . .	50 grams,	. . .	1 oz.
Sulphuric acid (commercial),	. . .	50 c.c.,	. . .	1 „
Water,		1000 „	. . .	20 ozs.

Dissolve the bichromate in the water, and when dissolved add the sulphuric acid in a thin stream, stirring the while. For some purposes it is convenient to use much more sulphuric acid.

Rinse well under the tap when clean. The solution, if no water is added to it, may be used over and over again until exhausted.

Perhaps it will be well to define what is meant by "washing." In regard to utensils it is used in the ordinary sense, but when employed in connection with prints and negatives, a wrong impression is often conveyed. When a photographer says "wash," he generally means "soak." In a recently fixed negative, for example, the "hypo." must be removed from the film by soaking it out. A constant diffusion goes on between the solution of "hypo." in the film and the clean water in contact with it. At first this diffusion proceeds very rapidly, and then more and more slowly as the "hypo." in the film becomes dilute. No advantage is to be gained, therefore, by allowing the water to run furiously over the surface of the plate, as force does not assist the operation, and the water must be left in contact with the film for a sufficient time to take up

its allowance of "hypo." Running water is a distinct advantage, although frequent changes and rocking of the dish do nearly as well; but the water may run as slowly as you please, and should flow into the upper part of the whole contents of the vessel, but out from the lower part. A syphon should be used to remove the water from all deep washing tanks.

Mention will be made directly of atoms and molecules, so that I had better explain what is meant by these terms, and by a chemical element. If pure iron is ground up very small and acted upon by the strongest forces that the chemist can bring to bear upon it, nothing but iron can be obtained from it. The substance cannot be split up into two other materials, so that chemists call it and all such substances "elements." If the powdered iron that was spoken of just now be examined under the microscope, it will be seen that the particles would bear splitting up very much smaller. Chemists have come to the conclusion, that if human eyesight and fingers were keen enough to go on splitting up these microscopic particles, a stage would be reached when the particles could be made no smaller. These ultimate particles are called "atoms." All the atoms of iron, for instance, may be considered as being exactly alike and of the same size and weight. As it is not possible to examine the actual atoms, equal quantities of the different elements are compared with one another.

In this way it is found that the iron atom is 56 times as heavy as the hydrogen atom, which, being the lightest, is called 1, and is used as the standard of atomic weight. The silver atom is 108 times as heavy as the hydrogen atom, so that the atomic weight of silver is 108, and that of iron 56. These atoms combine with one another to form "molecules," so that a molecule is compounded of atoms. The iron atom, for instance, may combine with another iron atom to form an iron molecule, or it may combine with one or more atoms of some other element, such as chlorine (see later), to form a molecule of iron chloride. Now I want you to realise that nothing ever happens by chance in chemistry. Similar quantities of the same substances, acting in the same way, always produce the same result, and *the same quantity of it*, as you will see directly.

For convenience, chemists employ a kind of shorthand, using symbols for the different substances. H stands for hydrogen and for 1 gram or ounce, or whatever it may be, of hydrogen; Fe (Latin, *ferrum*) stands for iron and for 56 grams, or whatever it may be, of iron, and so on. The following symbols for different elements will be used in this chapter; particulars of the others will be found in the index:—

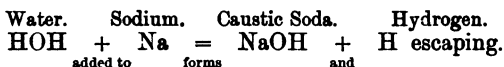
Name.	Symbol.	Atomic Weight.
Hydrogen,	H	1
Oxygen,	O	16
Nitrogen,	N	14

Sulphur,	.	.	.	.	.	S	32
Carbon,	.	.	.	.	.	C	12
Chlorine,	.	.	.	.	.	Cl	35.5
Bromine,	.	.	.	.	.	Br	80
Iodine,	.	.	.	.	.	I	126.5
Sodium,	.	.	.	.	.	Na	23
Potassium,	.	.	.	.	.	K	39
Silver,	.	.	.	.	.	Ag	108

Coal gas is a mixture of various inflammable gaseous materials, but amongst them contains a large proportion of a gas called hydrogen. When this burns, it combines with the oxygen in the air—another gas—to form water. If a cold plate or piece of metal be held for a second or two over a gas flame and then withdrawn, the surface will be coated with moisture (the soot need not enter into the question). It has been found, from a large number of experiments, that a particle of water consists of two atoms of hydrogen, each weighing 1, combined with one atom of oxygen weighing 16, and is represented chemically as HOH (or H_2O), the total weight ($1+16+1$) being 18. 61

Sodium is a metal, quite soft at ordinary temperatures, but its freshly cut surface is bright and metallic looking. If a piece about the size of a large pin's head be dropped into water, a great commotion ensues, and bubbles of gas are given off, which take fire if a light is applied to them, and sometimes do so on their own account. This gas is hydrogen. The atoms of sodium (Na) are turning 62

out half the hydrogen atoms from the water, thus :—



Instead of water there is now a weak solution of caustic soda, which turns red litmus-paper blue, changes acids into substances that are not acid but neutral, and is called an alkali. If more sodium be added to the solution, more hydrogen will be turned out, the alkaline solution becoming stronger, forming in the end a solid mass of caustic soda, which could be run into moulds to make the familiar white sticks.

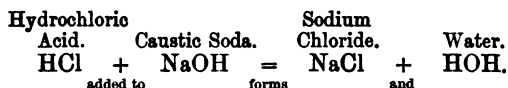
It has been shown that a particle or molecule, as chemists term it, of water (HOH) weighs 18. In caustic soda (NaOH) there is an atom of sodium (Na) occupying the place of one of the H's, weighing 1. Now an atom of sodium is twenty-three times as heavy as an atom of hydrogen, so that caustic soda (NaOH) weighs 40 (23 + 16 + 1). This means that if 23 grams, ounces, or lbs. of sodium were cut up into small pieces and dropped into 18 grams, ounces, or lbs. of water, 40 grams, ounces, or lbs. of caustic soda would be obtained, than which nothing could be simpler. All chemical formulæ can be expressed in actual weights in just the same manner.

The formulæ that appear so alarming are merely this convenient and scientific kind of shorthand, the key to which will be found on page 140.

Chlorine is a yellowish-green, very irritating gas. If the reader wishes to become acquainted with it, let him warm ten drops of hydrochloric acid with five drops of nitric acid in a test-tube or other glass vessel, when fumes of chlorine will be freely given off. This yellowish-green gas combines violently with hydrogen to form hydrochloric acid (HCl), one atom of the one combining with one atom of the other. What is ordinarily called hydrochloric acid, and purchased of a chemical dealer, is a solution of hydrochloric acid gas; this solution will be found to turn blue litmus red, to be intensely acid to the taste (dilute), and to be exactly the opposite of the alkaline caustic soda. e^s

If caustic soda be mixed with hydrochloric acid in proper proportions, a neutral liquid will be obtained. A great deal of heat is given out, and the experiment must be tried with dilute acid and alkali. The resulting liquid is called "neutral," because it is neither acid nor alkaline, and has no effect on litmus-paper; it is, in fact, a solution of a salt—common salt or sodium chloride. e⁴

What has just happened is represented in chemical shorthand thus:—



This is called an "equation," because there is an equal quantity of material on both sides, but it is

arranged differently. Whenever anything happens in chemistry, there is the same quantity of material at the end as there was at the beginning. Nothing is ever destroyed; the different parts are merely rearranged.

Now take a solution of silver nitrate! If you have the means of weighing and measuring accurately, make up a 1 per cent. solution of silver nitrate by dissolving 1 gram in 100 c.c. of distilled water; fill a burette with the solution and run exactly 34 c.c. into a dish or gallipot of some kind. Make up a 1 per cent. solution of sodium chloride (1 gram in 100 c.c.); put this in another burette, and out of this run 10 c.c. into the gallipot containing the 34 c.c. of silver nitrate. A white "precipitate" will form; shake the vessel round and allow the precipitate a few moments to settle to the bottom. Then add a few more drops from the sodium chloride burette. A fresh white precipitate will form and sink to the bottom. This precipitate will go on forming until 11.7 c.c. altogether of sodium chloride solution have been added. If the solution be now allowed to stand until the precipitate has settled, no more precipitate will form when more sodium chloride is run in. If the reader has not conveniences for measuring, he must take a small quantity of silver nitrate solution, and add solution of common salt in small quantities at a time until no more precipitate is thrown down.

To explain what has been happening, it is necessary

to say a few words about silver nitrate. Nitric acid contains one atom each of hydrogen and nitrogen and three atoms of oxygen. As hydrochloric acid is HCl, so nitric acid is HNO_3 . When silver (Ag) is dissolved in nitric acid, the silver takes the place of the hydrogen, producing silver nitrate (AgNO_3).

When the sodium chloride was run into the silver nitrate in the experiment, the sodium and the silver changed places.

Silver Nitrate. Sodium Chloride. Silver Chloride. Sodium Nitrate.
 $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$.

The white precipitate was silver chloride, and the sodium nitrate remained dissolved in the solution. Further, it was seen from the experiment that 11.7 parts of sodium chloride were just sufficient to cause all the silver in 34.0 parts of silver nitrate to precipitate as chloride. If the different parts of the equation are calculated out, it will be seen that this is the case.

$$\begin{array}{ccccccc}
 \text{Ag} & \text{N} & \text{O}_3 & + & \text{Na} & \text{Cl} & = & \text{Ag} & \text{Cl} & + & \text{Na} & \text{N} & \text{O}_3 \\
 108 + 14 + 48 & & & & 23 + 35.5 & & & 108 + 35.5 & & & 23 + 14 + 48 \\
 \hline
 170 & & & & 58.5 & & & 143.5 & & & 85
 \end{array}$$

So that 170 AgNO_3 requires 58.5 NaCl, or 340 requires 117. From this equation it will be seen also that from 170 parts of silver nitrate 143.5 parts of silver chloride can be obtained. This calculation, or similar calculations with bromide and iodide instead of chloride, are being gone through

constantly when making emulsions. Although tables are given to save time, every photographer should know how to work out the figures himself if necessary.

Potassium (K) is a very similar metal to sodium, and it is sometimes more convenient to use potassium salts, such as potassium bromide and potassium iodide, instead of sodium salts, but the calculations are exactly similar, using K (39) in place of Na (23).

Cut Bromine is a red liquid and iodine a brownish, rather metallic looking, solid. They resemble chlorine very closely, and silver bromide and iodide are very like silver chloride. Take two gallipots and place silver nitrate solution in each. Into one run a solution of potassium bromide, and into the other a solution of potassium iodide. A precipitate will be formed in each case; that with the bromide being yellowish-white (silver bromide), and that with the iodide being pale yellow (silver iodide). These experiments can all be performed in test-tubes, *i.e.*, thin glass tubes closed at one end, or in beaker flasks; the latter (fig. 3) are useful for many purposes in the work-room.

As silver chloride, bromide, and iodide resemble one another so closely in their chemical properties, they can often be substituted for one another partly or wholly without introducing any very great change in the result. In making emulsions for dry plates, or in preparing collodion for wet plates, these salts are introduced in varying proportions to suit the

subject. Accordingly it is important to know what quantity of chloride is equivalent to a certain quantity of bromide or iodide, and *vice versa*. This can be learned from chemical shorthand at once. The formulæ for the three compounds are AgCl, AgBr, and AgI. An atom of bromine (Br) weighs 80 and iodine (I) weighs 126.5; so that

Silver chloride, AgCl, weighs $108 + 35.5$ or 143.5
 „ bromide, AgBr, „ $108 + 80$ „ 188
 „ iodide, AgI, „ $108 + 126.5$ „ 234.5

From this it is clear that 143.5 parts of the chloride are capable of doing the same work as 188 parts of bromide or 235 of iodide. The following table gives equivalent quantities of these salts to save calculations.

TABLE III.—EQUIVALENT QUANTITIES OF SILVER SALTS.

Silver (Metallic).	Nitrate.	Chloride.	Bromide.	Iodide.
1	1.574	1.328	1.741	2.176
0.6358	1	0.844	1.106	1.382
0.7523	1.184	1	1.310	1.638
0.5744	0.904	0.763	1	1.250
0.4595	0.723	0.610	0.800	1

Take the three vessels containing the precipitates—silver chloride, bromide, and iodide—and decant off the liquid with the help of a glass rod as shown in the sketch (fig. 4). To the first add a few drops

Fig.

of ammonia solution; the silver chloride will dissolve completely. To this solution add a few drops of acid to neutralise the ammonia; the white silver bromide will reappear, showing that, although it is soluble in ammonia, it is insoluble in acids. To the bromide precipitate add a solution of what is generally known as hyposulphite of soda; the precipitate will dissolve completely. The other pre-



Fig. 3.

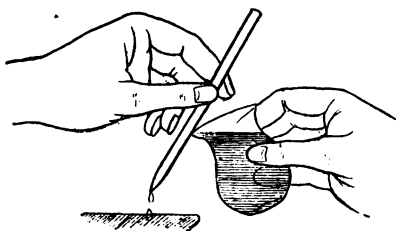


Fig. 4.

cipitate may be treated with potassium cyanide, with a like result.

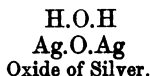
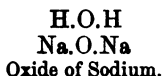
Now to go back to the first experiment, when metallic sodium was added to water, so that an atom of sodium took the place of an atom of hydrogen, forming NaOH instead of HOH . If the excess of water be driven off by heating the solution, or if enough sodium be added to combine with all the water, a solid mass of sodium hydrate (caustic soda, NaOH) will be formed. If more sodium be added to this and the mixture be warmed, the other

hydrogen atom will be turned out by the sodium, thus:—



This substance, Na_2O , is called "oxide" of sodium, and much resembles the hydrate or caustic soda in appearance.

Now add some caustic soda solution to a little silver nitrate solution—by a "little" is meant from half an inch to an inch of liquid in a small test-tube or measuring glass. A light brown precipitate will sink to the bottom. This light brown substance is oxide of silver, or Ag_2O , and is put together in exactly the same way as oxide of sodium.



The silver compounds must be left for a little while and something must be said about the salts of iron, which are not quite so simple as those of silver. First dissolve up a few of the green crystals of sulphate of iron or ferrous sulphate, as it is more correctly called. To some of this add a little caustic soda, and watch what happens: a precipitate is formed, first white, then green, and ultimately brown. If this white precipitate could be kept from changing whilst it was dried and heated, you would get an oxide of iron—"an oxide" because there are more than one. This oxide would be FeO , one atom of iron (Fe) being capable of turning out both atoms

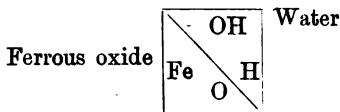
67.

of hydrogen from water, or replacing two atoms of silver, or two atoms of sodium, etc. The white precipitate was ferrous hydrate. As iron is capable of taking the place of two atoms of sodium, you have



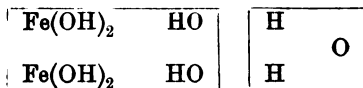
so that ferrous hydrate is $\text{Fe}(\text{OH})_2$.

When this hydrate is dried and heated, a particle or molecule of water splits off, leaving the oxide, FeO , thus:—



In actual practice, however, you have seen that the white precipitate turned green and then brown. The ferrous hydrate was using the oxygen of the air to convert itself into another hydrate containing more OH, viz., $\text{Fe}(\text{OH})_3$. From this you see that iron can combine with either two or three OH's, *i.e.*, can take the place of either two or three atoms of hydrogen or silver or sodium, etc. Consequently, ferrous iron is always hungry until it has got hold of the third OH, or whatever it may be. It is important that you should understand this thoroughly, as it is the basis of the development of negatives. In the solution, after the addition of the caustic soda to the ferrous sulphate, you had essentially (neglecting the sodium and the sulphate) water, oxygen from the

air dissolved in the water, and a substance—ferrous hydrate—ready to pick up any OH that might be available. The oxygen is anxious to combine with hydrogen to form water, so that you have ferrous hydrate and oxygen with a particle of water between, like a duck and a hen over a worm. The water comes in half, as the metaphorical worm would do; the iron gets its OH (hydroxyl), and the oxygen gets its hydrogen, and everybody is satisfied, thus:—



Any substance that is anxious to get hold of hydrogen acts like oxygen in presence of water, or, to put it in different words, is an oxidizing agent. Chlorine and bromine, for example, behave in this manner. If you had added chlorine or bromine to the ferrous hydrate, it would have gone brown at once. The action would have been complicated, however, by the hydrochloric acid formed (see page 19) dissolving the hydrate to make ferric chloride, in the same way that sodium hydrate with hydrochloric acid produced sodium chloride.

Now see what happens when ferrous sulphate is added to a silver salt, say silver nitrate: a black precipitate is formed. The iron, as it were, says to the silver, "You've got my NO₃; drop it!" And the silver has to drop it and become "reduced" to

metallic silver, whilst the ferrous iron appropriates the NO_3 to raise itself to the ferric state.

It is quite clear, then, that an oxidizing agent is a substance that is anxious to take up hydrogen, and, *vice versa*, a reducing agent is a substance that is hungering after oxygen. Hydrogen itself is a very powerful reducing agent. With metallic salts, oxidation raises them further from the metallic state; reduction robs them of whatever other substance, such as chlorine or nitric acid (nitrate), they are combined with, and brings them back wholly or partly to the simple metallic condition.

From the talk about ferrous and ferric salts, you have seen that chemical elements may combine in other proportions than one to one. Silver chloride contains one of silver to one of chlorine; ferrous iron takes two of chlorine; ferric iron, three of chlorine; in platinic chloride there is one of platinum to four of chlorine, and there are other compounds with a higher proportion of chlorine still. For convenience in chemical shorthand, the number of atoms of hydrogen an element is capable of replacing is denoted by dashes, thus:—

$\text{Ag}'\text{Cl}'$, Silver chloride.
 $\text{Fe}''\text{Cl}_2$, Ferrous ,,
 $\text{Fe}'''\text{Cl}_3$, Ferric ,,
 $\text{Pt}^{\text{iv}}\text{Cl}_4$, Platinic ,,

Sulphuric acid has the composition represented in chemical shorthand as H_2SO_4 , so that, as ferrous iron can replace two H's, the composition of ferrous

sulphate is FeSO_4 . The green crystals that you buy, or that would be obtained if you evaporated a solution of ferrous sulphate to a thick syrup and allowed it to crystallize, contain water, as do most crystals. In assuming the solid condition, many substances crystallize in two or three different forms according to the amount of water their particles entangle. Ferrous sulphate carries down with it seven molecules of water, so that the formula for the green crystals is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This is important, as, in making up percentage or other solutions, this water has to be taken into account. For instance, suppose a ten per cent. solution of ferrous sulphate is required. Then

$$\begin{array}{rcl} \text{FeSO}_4 (56 + 32 + 64) & = & 152 \\ 7\text{H}_2\text{O} (2 + 16) & = & 126 \\ \hline & & 278 \\ \hline \end{array}$$

So that 278 parts of the crystals only contain 152 parts of ferrous sulphate. To calculate how much FeSO_4 must actually be used, you make the proportion sum,

$$\begin{array}{ccccccc} & & \text{is to} & & \text{as} & & \text{is to} & & \text{the amount required.} \\ & & 152 : 278 & :: & 10 : x. \\ 278 \times 10 \div 152 & = & 18.3 \text{ parts as nearly as possible.} \\ \text{multiplied} & & \text{divided} & & \text{gives} & & & & \\ \text{by} & & \text{by} & & & & & & \end{array}$$

A few words now about acids! Several different acids have been mentioned, but they possess one feature in common; they all contain hydrogen. Acids are salts of hydrogen. Hydrochloric acid

(HCl) is hydrogen chloride just as AgCl is silver chloride; sulphuric acid being hydrogen sulphate. The last named acid contains two atoms of hydrogen, both of which can be replaced by a metal, and there are other acids, such as phosphoric acid (H_3PO_4), which contain more than two atoms of hydrogen. In the carbon or organic acids, such as citric or acetic acids, there are atoms of hydrogen that are not replaceable, and their formulæ are liable to confuse the reader, but in the last chapter (which see) the hydrogens that can be displaced by iron or sodium or silver, etc., to form salts are shown quite clearly.

With hydrochloric acid, where there is only one hydrogen, the latter must be displaced entirely, but with sulphuric acid, where there are two hydrogens, you may have either one or both atoms replaced by a metal. For instance, there are two sodium sulphates, thus:—

H_2SO_4 , Sulphuric acid.

NaHSO_4 , Acid sodium sulphate.

Na_2SO_4 , Neutral or normal sodium sulphate.

The salt in which only one of the hydrogens has been displaced has an acid character, as you would expect, and is called "acid sodium sulphate." You will understand from this that an "acid" salt means a salt in which the hydrogen is only partly displaced by metal. The term "bi" is used frequently instead of "acid," so that NaHSO_4 is generally called sodium bi-sulphate.

In salts that are derived from acids containing oxygen there is a possibility of reducing that oxygen. Sulphuric acid or a sulphate, for example, may be deprived of one or two atoms of oxygen, producing

H_2SO_4 , Sulphuric acid.
 H_2SO_3 , Sulphurous acid.
 H_2SO_2 , Hyposulphurous acid.

Their sodium salts are

Na_2SO_4 , Sodium sulphate.
 Na_2SO_3 , „ sulphite.
 Na_2SO_2 , „ hyposulphite.

This last salt is true sodium hyposulphite; the photographer's "hypo." is not hyposulphite of sodium, correctly speaking, but sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$.

From all this the reader will gather some idea of the way in which chemical compounds are named. The termination "-ide" signifies a salt consisting of a metal united with another element, such as silver chloride; "-ate" signifies a salt containing oxygen as well; "-ite" contains less oxygen than "-ate."

If "hypo" is put in front of the word, it means that the salt is below the "-ite" stage. The prefix "per" or "hyper" means above, so that a persulphate of sodium is richer in oxygen than sulphate of sodium.

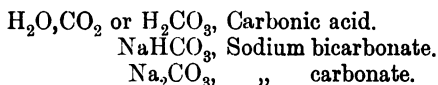
Having said so much about acids, it is necessary to devote a paragraph to alkalies. You have seen at the beginning of the chapter that caustic soda or

sodium hydrate is water in which one atom of hydrogen has been replaced by one of sodium. Caustic potash, or potassium hydrate, is exactly similar, potassium (K) taking the place of sodium. Caustic potash and caustic soda dissolved in water possess a peculiar "alkaline" taste, turn litmus-paper blue, and neutralize acids to form salts. An alkali, therefore, is a soluble hydrate. Nearly all hydrates and oxides, although not soluble in water, have an alkaline tendency, and possess some of the properties enumerated above.

Ammonia, properly speaking, is a gas, not a liquid. It is formed of one atom of the element nitrogen, which constitutes four-fifths of the atmosphere, combined with three atoms of hydrogen. This NH_3 dissolves in water with avidity, forming $\text{NH}_3\text{H}_2\text{O}$ or NH_4OH . Rather curiously this is a powerful alkali, and closely resembles caustic potash or soda in its action. So much is this so that NH_4 is called by one word, "ammonium," and NH_4OH is ammonium hydrate. The liquid ammonia of the druggist, then, is a strong solution of ammonium hydrate. This "ammonium" forms salts exactly like sodium or potassium, producing ammonium chloride, NH_4Cl , ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, etc.

As caustic potash, soda, and ammonia are such strong alkalies, when they unite with a weak acid their salts are alkaline. Carbonic acid is a weak acid, and sodium carbonate is strongly alkaline.

The bicarbonate, although it is theoretically an acid salt, is faintly alkaline. Carbonic acid, by the way, is formed whenever carbon (coke or charcoal) or any substance containing carbon is burnt in the air. Carbon (C) unites with two oxygens to make CO_2 , and when this gas dissolves in water carbonic acid is formed. The term "carbonic acid" is from long usage generally applied to the CO_2 gas, but all the carbonates are formed from CO_2 dissolved in water, thus,



Sodium carbonate is the compound used as an alkali in photography. It can be obtained perfectly dry, but the most convenient form is washing soda. The crystals of this material contain water in the same way that ferrous sulphate crystals contain water, the formula for washing soda being $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Now Na_2CO_3 adds up to 106 ($46 + 12 + 48$), and 10 of water make 180; so that, adding the two together, 286 of washing soda are equivalent to 106 of dry sodium carbonate, and this fact must be borne in mind when making up solutions.

This is a convenient place to say a few words about electro-chemistry. When two metals, such as zinc and copper, are joined together and placed in a liquid that conducts electricity, such as dilute

sulphuric acid, an electrical current is produced and flows from the copper or positive metal through the wire, or whatever it is that joins them, to the zinc or negative metal, then through the acid back to the copper again, completing the circuit. This arrangement is called an electric battery; various other combinations of metals are used in different batteries, but the principle is the same. It is not necessary to use two metals to produce an electric current, a metal and a solution of a metallic salt, or even two solutions separated by a porous partition, being sufficient to cause a current. It is evident that nearly every chemical change must produce an electric current, or *vice versa*, and it is difficult, if not impossible, to separate one from the other.

Now try this experiment: Make a little electric battery of a strip of zinc and a strip of some other metal, dipping in dilute acid in a jam-pot or something of the kind; connect the copper strip by a wire to another smaller strip of copper, and the zinc in a similar way to another little strip of zinc; allow the two latter strips to dip into a solution of sulphate of copper in a beaker or glass of some kind, so that you can see what is going on. In a few minutes, the zinc strip will have become coated with copper, and if you had weighed the copper strip before the experiment, you would find that some of it had dissolved. This is the principle of electro-typing, electro-plating, electro-gilding, and

so on. If you had had a convenient solution of silver instead of the sulphate of copper, silver would have been deposited on the zinc.

As you will see in the next chapter, much of what goes on during development resembles electroplating. In the solution a kind of "ladies'-chain" is taking place, the atoms of metal travelling in the direction of the current, to be deposited finally on the negative electrode or terminal of the wire connected with the zinc of the battery or what corresponds to it. In developing, it is very possible that each particle of reduced silver in the latent image acts as the terminal of a tiny electric battery or "couple," as it is called, and the silver from the surrounding silver salts is deposited on it to build up the visible image.

CHAPTER III.

THE CHEMISTRY OF THE PHOTOGRAPHIC IMAGE.

THE chemistry of the different processes for producing and developing a latent image are so interwoven that it is convenient to talk about them together; the composition of the different plates and developing materials will be considered separately afterwards. First of all, however, it will be necessary to say a few words about the photo-chlorides and kindred salts of silver.

The photo-chlorides of silver, which Carey Lea did so much to investigate, are the compounds produced by the action of light or reducing agents, such as ferrous sulphate, on silver chloride. They contain less chlorine than silver chloride, and may be regarded as stepping-stones between silver chloride and metallic silver. There seems to be a considerable number of them, and they vary in colour from white, through flesh-colour, pink, rose, copper-red, reddish-purple and chocolate, to black. They appear to be permanent if kept in the dark, but change rapidly in the light. More about these interesting

compounds and about some curious and beautiful forms of metallic silver, which are soluble in water, will be found in Chapter VII.

The photo-bromides and photo-iodides resemble the photo-chlorides very closely. In all cases the presence of soluble chlorides, bromides or iodides, such as sodium chloride or potassium bromide, etc., in solution hinders the formation of the photo-salts, an acid having the same effect, whilst an alkali or reduced silver hastens their formation.

To pick up the thread where it was dropped at the end of the last chapter, Hunt found, in the early days of photography, that invisible images could be produced by heat, and that these could be developed subsequently. If a hot coin be held close to a piece of clean glass, the image of the coin can often be reproduced by breathing on the glass. The action is properly electrical, but in any case there is a selective action, so that the moisture sticks to one part and not to another. Hunt used polished metal, and developed his images with mercury vapour, the principle being the same.

In Daguerre's process a polished silver plate was exposed to iodine vapour, so as to form a thin film of silver iodide on the surface. This plate was then exposed in the camera, and developed with mercury vapour. In this case the result was very different from the heat or "thermographic" images. The light in the bright parts of the image thrown by the lens had reduced the silver iodide in the thin

film on the surface, and the liberated iodine probably acted on the metallic silver just behind to form more photo-iodide, thus intensifying the effect of the light. The mercury vapour combined chemically with the reduced parts of the plate, so that a visible image was formed. This was fixed and toned with gold salts.

So far you have seen, first, a mechanical effect caused by heat, and developed mechanically; secondly, mechanical effect caused by light, ending in chemical action, and extended or developed by chemical action. In the former case the invisible or latent image was due probably to different electrical conditions on different parts of the surface. In the latter case, you have every reason to suppose that the latent image was composed of reduced silver iodide or photo-iodide. I should like to take the opportunity here of impressing on the reader's mind the fact that photographic action is not yet thoroughly understood. Even in such a comparatively simple affair as a Daguerreotype plate, the latent image cannot be taken out and examined. In wet plates, and more especially dry plates, the conditions are much more complicated, so that the difficulty in finding out what happens is greatly increased. Consequently, scientific guesswork has to be brought to the aid of the investigator; the guesswork is of a very shrewd order, but it is guesswork none the less. When you consider that in a wet plate, for example, you have an almost microscopically thin,

and by no means simple, film to start with, and that only the outermost particles of this thin film appear to be affected directly by the light, you will see that it is not easy to lay down the law as to what happens in the film.

A wet plate after exposure consists essentially of a film of collodion containing silver iodide, a part of which has been acted upon by the light, and this is covered with a layer of silver nitrate. The developer, made up of a solution of ferrous sulphate containing a little acid—generally acetic acid—is poured over this. Ferrous sulphate alone would reduce the silver nitrate at once, covering the plate with a black deposit of metallic silver; but the presence of the acid hinders this action, so that the reduction only proceeds slowly. Probably the first action of the developer is to reduce to the metallic state the photo-iodide that has already been acted upon by the light. This forms a nucleus for the deposit of silver from the reduced nitrate, in a similar manner to the selective action in the thermographic image, and this reduced silver is built up on the latent image forming the visible image of the wet plate.

As development proceeds, the ferrous sulphate becomes oxidized (see p. 27) and loses its reducing power, so that the formation of the image progresses more and more slowly, or, in photographic language, the developer becomes more and more restrained. It is obvious that if any substance be present that will absorb the acid given off by the silver on reduc-

tion, the formation of the image will go on more rapidly. In 1866 Poitevin tried the experiment of squeezing a collodion film containing silver iodide, free from excess of nitrate, on to a silver plate, and treating a glass plate in a similar manner. Both were exposed to light and developed. The film on the silver plate showed a considerable image, being very much denser than that on the glass plate, but the latter did show a slight image. From this it is clear that an image of reduced silver can be formed even when there is nothing to absorb the iodine or whatever it may be that is given off. It is conjectured that in such a case a compound must be produced similar to KI_3 —the dark substance obtained on dissolving iodine in potassium iodide. The statement that an absorbent of iodine, chlorine, or acids, such as metallic silver, hastens development, however, is amply proved by this experiment.

In making a wet plate for use, collodion (see Chap. XIV.) is iodized by dissolving soluble iodides, or even iodine itself, in the collodion. Except for process work, it is usual to employ bromide as well as iodide. The latter alone gives a hard negative, and bromide alone a flat detailed negative; the proportion of the two can be varied to suit the subject. The bromides and iodides of cadmium and ammonium are those generally used.

The glass plates to be coated must be carefully cleaned and polished with tripoli, whiting, or rouge, or better, by soaking in sulphuric acid and bi-

chromate of potash (see p. 14); then edged with india-rubber solution and given a first coat or substratum of albumin or gelatin to which a few drops of ammonia have been added. This preliminary edging and coating is to prevent the collodion slipping or coming away from the glass. The iodized collodion is poured on to the plate and distributed evenly by rocking, the excess being drained off at one corner. In subsequent operations this corner should always be kept at the bottom. The plate is then immersed in a bath of silver nitrate, which is generally made faintly acid with nitric acid. The silver nitrate is converted into bromide and iodide (see p. 22), and the plate is ready for use. As this iodide is soluble in silver nitrate, the silver bath is saturated with iodide before use by adding a few grains of potassium iodide, and filtering off any undissolved precipitate of silver iodide.

After exposure the plate is developed by pouring over it a solution of ferrous sulphate made acid with acetic acid. Ammonio-ferrous sulphate and copper sulphate are used sometimes in the developer; the former replaces part of the ferrous sulphate, acting more slowly, and the latter acts as a restrainer.

The positives on glass, made by the wet plate process, are really negatives which receive a less exposure in the camera than is required for the ordinary negative, and are coated on the film side

with black varnish after development. Consequently the black of the varnish shows through the transparent parts of the plate, and the silver deposit shows white by reflection, so that the negative is turned into a positive.

The various formulæ for producing a finished wet plate negative are as follows, those marked with an asterisk being employed at the Bolt Court Process School:—

*The Substratum.**

Sheet gelatin,	2.5 grams,	22 grs.
Ammonia .880,	4 c.c.,	40 minims.
Water (distilled),	1000 „	20 fl. ozs.

*Rubber Solution for Edging.**

Pure rubber cut into small pieces,	1 gram,	20 grs.
Benzole,	100 c.c.,	5 ozs.

*Silver Bath for Sensitizing.**

Silver nitrate,	68 grams,	600 grains.
Water (distilled),	1000 c.c.,	20 fl. ozs.
Pot. iodide (10% solution),	1 „	60 minims.
Sodium carbonate cryst.,	3.5 „	30 grs.

Dissolve the silver nitrate in one-quarter of the total water, then add the potassium iodide, and shake; when the precipitate has dissolved, add the sodium carbonate dissolved in part of the water, shake, and add the rest of the water. Acidify with a few drops of 10% nitric acid.

*Collodion.**

Plain collodion,	750 c.c.,	15 ozs.
Iodizer (B solution),	250 „	5 „

Iodizer (B. Solution).

Iodine,	45 gram,	2 grs.
Alcohol (ethyl),	100 c.c.,	1 oz.

The iodizer must be mixed with the collodion in the proportion given, at least 24 hours before use. Store in a cool place, and do not disturb the sediment.

Collodion (another Formula).

Plain collodion,	100 c.c.,	1 oz.
Cadmium iodide,	1 gram,	$\frac{1}{2}$ grain.
Ammonium iodide,	7 „	3 grains.
Ammonium bromide,	4 „	$1\frac{2}{3}$ „

The iodides and bromide may be dissolved in the collodion, which is then suitable for general purposes. The proportions can be varied to suit the subject in accordance with the following tables, remembering that cadmium has a tendency to make the collodion granular. The table of chlorides is added for convenience.

TABLE IV.—EQUIVALENT QUANTITIES OF DIFFERENT BROMIDES.

Bromine.	Am- monium. Bromide.	Potassium Bromide.	Sodium Bromide.	Cadmium Bromide + 4H ₂ O.	Zinc Bromide.	Silver Bromide.
1	1·225	1·488	1·287	2·150	1·406	2·350
0·816	1	1·214	1·055	1·754	1·147	1·918
0·672	0·823	1	0·865	1·445	0·945	1·579
0·777	0·952	1·156	1	1·671	1·092	1·826
0·465	0·570	0·692	0·599	1	0·654	1·092
0·711	0·871	1·058	0·915	1·529	1	1·670
0·422	0·521	0·633	0·548	0·914	0·600	1

TABLE V.—EQUIVALENT QUANTITIES OF DIFFERENT IODIDES.

Iodine.	Am- monium. Iodide.	Potassium Iodide.	Sodium Iodide.	Cadmium Iodide.	Zinc Iodide.	Silver Iodide.
1	1·142	1·307	1·181	1·441	1·255	1·853
0·876	1	1·145	1·035	1·262	1·099	1·624
0·765	0·874	1	0·903	1·102	0·960	1·418
0·847	0·967	1·107	1	1·220	1·063	1·570
0·694	0·793	0·907	0·820	1	0·871	1·286
0·797	0·910	1·042	0·941	1·148	1	1·477
0·539	0·599	0·706	0·637	0·777	0·678	1

TABLE VI.—EQUIVALENT QUANTITIES OF DIFFERENT CHLORIDES.

Chlorine.	Ammonium Chloride.	Sodium Chloride.	Potassium Chloride.	Cadmium Chloride.	Silver Chloride.
1	1.507	1.648	2.101	2.575	4.042
0.663	1	1.093	1.394	1.710	2.682
0.607	0.914	1	1.275	1.564	2.453
0.475	0.717	0.784	1	1.226	1.923
0.388	0.584	0.639	0.818	1	1.570
0.247	0.373	0.408	0.520	0.630	1

If the collodion becomes too thick it may be "thinned" by adding a little of a mixture of 2 parts ether (.730) to 1 part alcohol (.805). In the wet plate process methylated alcohol and ether must not be used on any account.

*Developing Solution for Negatives.**

Ferrous sulphate, 34.5 grams,	. 300 grains.
Acetic acid glacial, 52 c.c.,	. 500 minims.
Rectified spirit, . 31 "	. 300 "
Water (distilled), 1000 "	. 20 ozs.

Developing Solution for Positives.

Pyrogalllic acid, 25 grams,	. 5 grains.
Acetic acid, . 4 c.c.,	. 100 minims.
Alcohol, . 5 "	. 120 "
Water, 100 "	. 5 ozs.

Fixing Solutions.

A. Potassium cyanide,	. 50 grams,	. 1 oz.
Water,	. 1000 c.c.,	. 20 ozs.

Take care that the cyanide is fresh.

B. Sodium thiosulphate (hypo.), 200 grams, 4 ozs.
Water, 1000 c.c., . 20 „
Either A. or B. may be used.

For intensification and reduction see Chap. VI. Further information about the wet plate process will be found in *Wet Collodion Photography*, by Charles W. Gamble.

The dry plate differs from the wet plate in many important respects. Silver bromide and a little iodide, or rather the materials to produce these—silver nitrate and potassium or ammonium bromide and iodide—are incorporated in an emulsion of gelatin, which is spread on glass plates or some other stiff material, such as celluloid, and allowed to dry. Collodion is sometimes employed instead of gelatin; the first dry plates having been made of collodion emulsion before gelatin was thought of. Before coating the plates, all excess of potassium and ammonium bromides and iodides, etc., are removed from the emulsion by prolonged soaking in water, the sensitiveness of the plate depending to a large extent on the thorough removal of these salts.

After exposure to light in the camera quite a different state of things exists to that on the wet plate. The silver salt (bromide mostly) is imbedded in gelatin, and is, therefore, much less open to attack by the developer, and there is no silver nitrate present. Two consequences arise from this: The silver image cannot be built up above the

latent image, as, in the absence of silver nitrate, there is no material to build from, so that the image must be formed from the silver bromide in the emulsion; moreover, the silver image is sunk downwards into the film instead of being built up above the latent image. Secondly, as no easily reducible silver salt is present, much more powerful developers or reducing agents can be used than sulphate of iron or other ferrous salts.

Although a further reference will be made to gelatin in the chapter on developers, in connection with pyrogallie acid, etc., a few words here about the complications introduced by the gelatin will not be amiss. In the first place, gelatin is a most complicated body itself, containing carbon, hydrogen, nitrogen, and oxygen, and its chemical structure is not known, so that when other substances, such as silver bromide, are mixed with it, complicating matters still further, it is not easy to find out exactly what happens. Either the silver bromide, before exposure, may lie perfectly inert, like so much shot in the gelatin, or it may combine bodily with the gelatin, or some interchange may take place between them; the combination, if it exists, is probably a loose one. In any case the ultimate effect is to allow the silver bromide to present a large surface to the action of the light. The process of stewing the emulsion or mixing ammonia with it, both of which have such a strong effect in adding to the sensitiveness of the plate, probably

act by causing a most intimate mixture of silver bromide and gelatin. When the plate is exposed, and still more when it is developed, the gelatin probably increases the sensitiveness by absorbing the free bromine when the bromide is reduced, in the same way that the metallic silver acted in Poitevin's experiment.

It is a doubtful point whether the silver bromide that has not been touched by the light, as, for example, the deeper parts of the film in an under-exposed plate, can be reduced by the developer, so as to help in building up the image. As the reader probably knows from bitter experience, the shadows and detail in the half-tones of a badly under-exposed plate remain absolutely unreduced, even after prolonged development. On the other hand, Abney tried the experiment of exposing a gelatino-bromide plate in the camera, and then covering it with a collodio-bromide emulsion. On development, the two films were separated, and it was found that each contained an image, so that, whilst the image was developing downwards in the ordinary way in the gelatino-bromide film, it was being added to from above by the silver bromide in the superposed film that had never seen the light. This result was confirmed by an experiment of Eder's, who succeeded in developing the image completely through a very thick and opaque film. When something is known with certainty about the nature of the latent image, it will be possible perhaps to say what is the correct view.

A collodion dry plate is made as follows :—

- | | | |
|-----------------------------|-------------------------------|-------------------|
| A. Pyroxyline (see p. 128), | 3 grams, | . 40 grains. |
| Alcohol (.820), | 30 c.c., | . 1 oz. |
| Ether (.730), | 60 c.c., | . 2 ozs. |
| B. Zinc bromide, | 3 grams, | . 40 grains. |
| Alcohol, | 1 c.c., or sufficient to dis- | |
| | solve the solid. | |
| Nitric acid, | 2 drops, | . 2 drops. |
| C. The same as B. | | |
| D. Silver nitrate, | 9 grams, | . 130 grains. |
| Water (warm), | 7 or 8 c.c., | $\frac{1}{4}$ oz. |
| Alcohol (warm), | 20 c.c., | $\frac{3}{4}$ oz. |
| Nitric acid, | 4 drops, | . 4 drops. |

Add the alcohol after the crystals have dissolved, and mix thoroughly.

When all is ready, put A in a wide-mouthed bottle sufficient to contain the whole; add B, and shake round. To the mixture add two-thirds of D, shaking round the while; then the whole of C, still shaking or stirring; then the remainder of D.

The emulsion may be used as it is or washed. When the plate, which must be edged with rubber as described in the wet plate process, has been coated by pouring the emulsion in a puddle in the middle, and making it flow all over the surface by tilting, it is allowed a few seconds to set, and is then washed by pouring water over it. This removes any soluble salts and renders the emulsion more sensitive.

Any weak developer (1 grain of pyro. to the oz., for example) may be used with these plates, and they may be fixed with potassium cyanide or sodium

thiosulphate (hypo.), as given for wet plates, preferably the former. The plates should be under-developed, as compared with gelatin dry plates, and then intensified (see Chap. VI.).

There are numerous formulæ for making gelatin dry plates, and the proportions of bromide and iodide vary according to the object for which the plates are intended to be used. The following formula,* due to R. Child Bayley, may be taken as an example of a gelatin bromo-iodide emulsion :—

A. Potassium bromide,	. 43 grams, 1½ ozs.
Distilled water up to	. 300 c.c., . 10 „
B. Silver nitrate, re-crystallized,	52 grams, 1¾ „
Distilled water up to	. 360 c.c., . 13 „
C. Potassium iodide,	. 1·6 grams, 25 grains.
Distilled water up to	. 60 c.c., . 2 ozs.

The proportions in these stock solutions are sufficient to make twelve batches of emulsion of half-a-pint each. Solution B should be rendered faintly acid to litmus-paper by adding two or three drops—not more—of acetic or nitric acid.

For use take—

- A. 75 c.c. (1¾ ozs.) containing 10·75 grams of potassium bromide.
- B. 90 c.c. (3¾ ozs.) containing 13 grams of silver nitrate.
- C. 15 c.c. (5 drams) containing 0·4 grams of potassium iodide.

* A full account of emulsion making, from which this formula is taken, will be found in Vol. II. of *The Photogram*, p. 152. Other formulæ, varied to suit the most exacting tastes, will be found in the different year books of the photographic journals.

A is placed in a large (20 oz.) flask, B in a smaller flask. Two grams of hard (Heinrich's) gelatin are weighed out and allowed to soak for an hour in the cold bromide solution in the larger flask. Both flasks are brought to 160° F. by placing in a saucepan half full of hot water, and testing with a thermometer. The contents of the smaller flask are then added in small quantities at a time to the gelatin and bromide in the larger flask, shaking the while. When the whole mixture is made, C is added, and the emulsion is placed in a covered earthenware jar to stew in the saucepan for an hour or so. The jar is supported by passing through a tin plate on the top of the saucepan, so that the bottom of the jar is about an inch from the bottom of the saucepan. At this point the emulsion should be tested by placing a drop on a piece of clean glass, taking it out of the dark room, where all the operations except the weighing and making up of the stock solutions are conducted, and looking through it at a candle flame. The emulsion should not appear gritty or strongly coloured.

After stewing in water, boiling gently for an hour or so, until it appears almost blue on examining a drop by the candle flame, the emulsion is allowed to cool, 10 grams more gelatin, which have been soaking in cold water for an hour, are added, and the whole well stirred until dissolved, when it is allowed to set. The cold emulsion is washed to soak out any soluble bromide, iodide, and nitrates, by squeezing it

many times through net or canvas under water. The emulsion is then warmed to 120° F., when the following is added, a few drops at a time, and the whole filtered through calico or chamois leather:—

Chrome alum (1 per cent. solution), 10 c.c., 3 drams.
Alcohol, 40 c.c., 1½ ozs.

The plates to be coated must be cleaned thoroughly by washing with strong soda, rinsing well, and allowing to dry. It does not pay, as a rule, to re-coat old negative glass. The coating may be performed with emulsion warmed up again to 105° F., in a somewhat similar manner to that described under wet plates. More material, however, must be run on to the plate, and very little need be drained off. The plate is rocked for some time, and then placed on a carefully levelled piece of glass to set. Drying must be performed in a dark room or well-ventilated cupboard as free as possible from dust.

NOTE.—*Never pack plates in newspaper* under any circumstances, as the print will be reproduced on development. Grooved cardboard boxes form the best packing. Turpentine, drying oils, varnishes and many other substances act upon an undeveloped dry plate, and care must be taken not to use these materials in the camera or double-back, or to pack plates in boxes containing them.

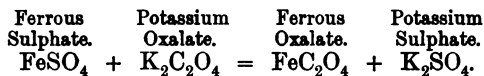
CHAPTER IV.

DEVELOPERS.

By this time the reader understands a good deal about the general principles of development. So far, however, acid iron developers only have been talked about. In a gelatin dry plate there is no easily reducible silver nitrate present, and the silver bromide itself is protected to some extent by the gelatin, so that much more powerful developers can be used than with wet plates, and alkalies can be introduced, which adds greatly to the rapidity of the plates.

The acid iron developer is very suitable for gelatin plates, giving very vigorous negatives, although it is necessary for the exposure to be correctly made. This developer is used in most standard work, as it causes no stain in the film. The following is the standard formula used in speed-testing on the Hurter and Driffield system, which will be referred to again directly. The formula, which works excellently, is due to Mr Cadett.

Ferrous oxalate is the iron salt used as a reducing agent; instead of the oxalate itself, however, the materials for making the oxalate, namely ferrous sulphate and potassium oxalate, are employed.



The potassium sulphate produced does not interfere with the development.

Ferrous Oxalate Formula.

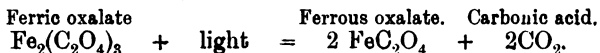
- A. Neutral oxalate of potassium, 200 grams, 1 part.
Distilled water, . . . 800 c.c., . 4 parts.
- B. Sulphate of iron, . . . 100 grams, 1 part.
Citric acid, . . . 1 gram, $\frac{1}{100}$ „
Distilled water, . . . 300 c.c., . 3 parts.
- C. Potassium bromide, . . . 1 gram, 1 part.
Distilled water, . . . 100 c.c., 100 parts.

For test use take A, 100 parts; B, 25 parts; C, 10 parts, in the order named. Make the developer up to a temperature of 65° F. and develop for five minutes; then, without washing, fix in a bath of sodium thiosulphate (hypo.) made up of 1 part to 3 parts of water; then, after thorough washing, place the plate in a 2% solution of hydrochloric acid to remove lime or other stains, and finally wash well.

The addition of a few drops of 1% sodium thio-

sulphate (hypo.) solution to each ounce accelerates the development of under-exposed plates when using a ferrous oxalate developer. The exact action is not known.

When using the above formula for ordinary studio or landscape work, it is a convenient plan to commence development with an old developer. This contains bromide from the reduction of the silver bromide in the film, so that there is no occasion to add bromide when working with an old developer. Many photographers stand the bottle containing the old developer in the sun to regenerate it, the light reducing the ferric oxalate to ferrous oxalate, which can be used over again.

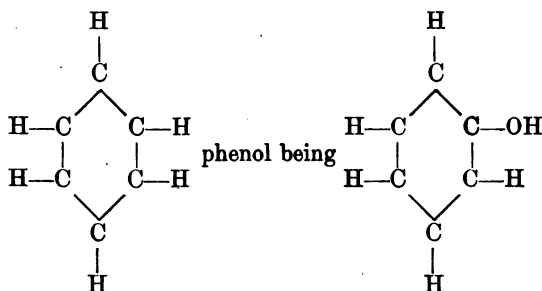


In the directions given above for using the ferrous oxalate developer, the correct temperature for development was stated to be 65° F. For standard work, such as testing the speed of plates, it is necessary to have the temperature as uniform as possible, and even in ordinary work, although excessive accuracy need not be observed, it is well to always develop as far as possible at the same temperature. Many photographers know the importance of employing a thermometer, but many others fail to realise the marked effect increase of temperature produces in hastening development.

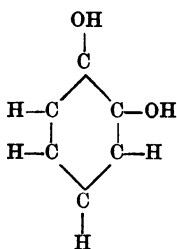
In some experiments made recently by the author, a difference of 15°—from 55° to 70° F.—caused an increase in the density of about one-third. From this it is clear that an under-exposed plate should be developed with a warm developer at, say, 70° F., and an over-exposed plate with a cold developer at, say, 45° to 55° F.

This is a convenient stage to talk about restrainers. It was seen (p. 37) that all soluble haloid salts (chlorides, bromides, and iodides) had a tendency to hinder the reduction of the bromide and kindred salts of silver. As any soluble haloid can be used, common salt may be used as a restrainer in the absence of potassium bromide. The reason why acids act as restrainers was explained on page 40. It is advisable to always work with some bromide in the developer, as otherwise the image comes up much too quickly, and the silver is apt to be reduced to a greater or lesser extent over the whole plate, causing "fog" and obscuring the finer detail.

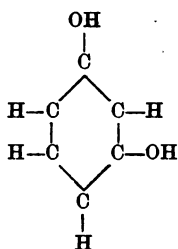
All the organic developers in general use bear a close chemical resemblance. Phenol (carbolic acid) is the base of them all, and phenol itself is benzene in which one hydroxyl (OH) has taken the place of one atom of hydrogen. Benzene, C_6H_6 , is always represented in chemistry like this,—



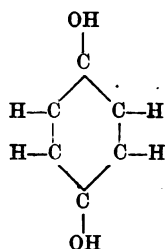
Pyrocatechin, resorcin, and hydroquinone are di-phenols, *i.e.*, they contain two OH's,



Pyrocatechin.
1·2



Resorcin.
1·3



Hydroquinone.
1·4

the difference being that the atoms are arranged differently, all three compounds having the formula $C_6H_4(OH)_2$.

Pyrogallie acid is a tri-phenol, having the formula $C_6H_3(OH)_3$, and is still the most extensively used of all developers. It is very soluble in water,

forming a 40 per cent. solution when saturated. It is soluble also in alcohol, ether, and glycerin. Like phenol (carbolic acid), it is not a true acid, such as sulphuric acid, and its proper chemical name is pyrogallol. It does form a combination with alkalis, however, and in this condition is a very powerful reducing agent. If left exposed to the air, it absorbs oxygen rapidly, turning first yellow, then brown, and finally black. The exact nature of the oxidation compounds formed are not accurately known. These brown products have a strong staining action on the gelatin, so that under-exposed negatives are much more liable to be stained, as not only are they in the developer for a much longer time, but the pyrogallate (*i.e.*, the compound of the pyrogallic acid with the alkali) is much more highly oxidized through contact with the air all the while. It has been found that a sulphite has the power of preventing this staining to a large extent. Sulphite of soda, $\text{Na}_2\text{S}_2\text{O}_3$, is generally employed, but sometimes the metabisulphite of potassium ($\text{K}_2\text{S}_2\text{O}_5$) takes its place. The drawback to the last-named is that it renders the solution very acid after a short time. Only one quarter the amount of metabisulphite is required, as compared with the crystallized sulphite.

As regards the influence of the quantity of sulphite in the developer on the resulting negative; sulphite has a distinct restraining action on the actual deposit of silver, and if a very large proportion of sulphite be present, the developer almost

steps working. The diminution of the yellow stain in the negative, however, is very marked as the sulphite is increased. The reduction in the quantity of sulphite from 5 to $2\frac{1}{2}$ grains to the fluid ounce of developer, in some recent experiments by the author, doubled the yellow stain in the dense part of the experimental plate, and increased it by about four times in the lighter portions. The entire absence of sulphite in another part of the same plate caused three times the stain in the denser parts, and about five times in the lighter parts, as compared with that portion of the plate developed with 5 grains to the ounce. Alfred Watkins and others have shown that this "pyro-stain" has an important influence on the printing value of the negative, so that it is better to use sufficient sulphite, say 4 grams to the 100 c.c. or 20 grains to the ounce, to practically eliminate the staining altogether. Some photographers have an affection for the yellow stain, and think it improves the "quality" of the negative. This may be true in cases of hard negatives, but the photographer should have complete command of his plate in the same way that the engine-driver has of the various levers that control the engine. If staining is allowed to creep in, the result becomes largely a matter of chance. For the same reason, the photographer should understand the effect of, and have under his command, each separate constituent of his developer, for these are the levers, so to speak, that control the photographic negative.

Ammonia solution or the carbonates of sodium and potassium are the alkalies employed in developing with pyrogalllic acid. Ammonia, although it is still largely used, especially by professional portrait photographers, seems unsatisfactory, because the ammonia evaporates from the solution during development, so that the developer grows continually weaker in alkali; the original concentrated solution itself is always varying in strength. Besides this, it must be a very bad thing for other plates or sensitive material to be in a room reeking with fumes of ammonia, which combine with any acid fumes that may be about, and deposit over everything in minute crystals.

Potassium carbonate possesses no advantage over sodium carbonate, except that it is much more soluble, which is an advantage in making up very strong solutions, but has the drawbacks that it is much dearer, is more difficult to obtain, and more of it is required in the developer.

Sodium carbonate is the most convenient alkali to use. Ordinary washing soda is the form generally employed, but there are two other forms that can be used equally well, namely, the monohydrated sodium carbonate and dry powdered sodium carbonate. The former of these two has recently been introduced commercially, so that it is well to include it. The latter is, or should be, pure sodium carbonate, Na_2CO_3 . The following table gives the equivalence of the three carbonates to one another

and to sodium hydrate (caustic soda), which may be useful with other developers.

TABLE VII.—EQUIVALENCE BETWEEN CAUSTIC SODA AND CARBONATES OF SODA.

Dry Sodium Carbonate.	Monohydrated Sodium Carbonate.	Washing Soda.	Caustic Soda.
1	1.17	2.70	0.76
0.85	1	2.30	0.64
0.37	0.43	1	0.28
1.32	1.55	3.35	1

It is convenient to know that bicarbonate can be converted into normal (dry) carbonate of sodium by heating it strongly, or by boiling its solution for some time. Sixteen parts of the bicarbonate are equivalent to ten parts of the ordinary dry carbonate.

Increase of alkali has a strong effect in hastening the rate of development all over the plate, excess causing fog.

Variations in the quantity of the pyrogalllic acid itself are important. It must be remembered that excess of pyrogalllic acid acts as a restrainer unless the alkali is increased in the same proportion. In some recent experiments the author has found that the greatest density was obtained with the pyrogalllic acid and alkali in proper chemical proportion (2 grains "pyro." to 7 grains washing soda). Half this quantity of pyro. (1 grain to the ounce), the alkali

remaining the same, gave less than half the density in the high lights of the negative, and only one-fifth or one-sixth in the shadows. When the pyro. was increased by a half (*i.e.*, to 3 grains) there was a distinct falling-off in the density, as compared with the rightly proportioned developer, to three-quarters in the high lights, and about the same in the shadows. When the pyro. was doubled (*i.e.*, 4 grains to the ounce) without change in the alkali, the result was practically the same as if one grain to the ounce had been used, showing the strong restraining action of the pyrogalllic acid. As the shadows were restrained more in proportion than the high lights, a considerable excess of "pyro." over alkali is clearly an advantage in developing an over-exposed plate. The effect of bromide in this direction, however, is almost the same. With these experiments in varying the quantity of pyrogalllic acid in the developer, it was found that the yellow stain did not increase with the "pyro." by any means, appearing to bear little relation to it, but followed the density of the silver deposit very closely.

As regards the composition of the developer, every photographer must be a law unto himself. The developer must be handled according to the exposure of the plate and the result the worker desires to obtain. The formulæ given by plate makers are, as a rule, needlessly complicated. The following is a good, sensible formula, which will work well with any plate:—

Pyrogallie acid,	.5 gram,	. 2 grains.
Sodium sulphite (crystals),	4.0 ,,	. 20 ,,
Sodium carbonate (crystals),	1.5 ,,	. 7 ,,
Potassium bromide, .	.25 ,,	. 1 ,,
Water up to	100 c.c.,	. 1 oz.

Unless a large number of negatives are to be developed, it is much better to use dry pyrogallie acid, weighing out sufficient for each small batch of plates before commencing development, and making it into a ten per cent. solution. The other materials may also be used conveniently in the form of ten per cent. solutions. The quantities to be taken to make up the above developer would be:—

Pyrogallie acid 10%,	. 5 c.c.,	. 20 minims.
Sodium sulphite 10%,	. 40 ,,	. 200 ,,
Sodium carbonate 10%,	. 15 ,,	. 70 ,,
Potassium bromide 10%,	. 2½ ,,	. 10 ,,
Water up to	100 ,,	. 1 oz.

It is convenient, as a rule, to add half the alkali at the beginning, and the remaining half as experience dictates. If the sky and high lights appear to be growing too dense, the full quantity, and even an excess, of alkali should be added immediately.

In the following formula ammonia takes the place of sodium carbonate, ammonium bromide being used instead of potassium bromide.

Pyrogallie acid, . . .	.25 gram,	. 1 grain.
Sodium sulphite, . . .	1.2 ,,	. 5 ,,
Ammonium hydrate, . . .	.6 c.c.,	. 2.5 minims.
Liquor ammoniæ (.880) }		
Ammonium bromide, . . .	.25 gram,	. 1 grain.
Water up to	100 c.c.,	. 1 oz.

Ten per cent. solutions may be used as recommended in the previous formula. When large quantities are required, the sulphite and the pyrogalllic acid may be incorporated into one stock solution in the proportion of—

Pyrogalllic acid,	50 grams,	.	.	1 oz. (avoir.).
Sodium sulphite,	250 „	.	.	5 „ „
Water up to	1000 c.c.,	.	.	20 „ „

For use take 20 minims of the stock, 4 drams of 10% ammonia, and 10 minims of 10% ammonium bromide with water to make up one ounce. If a stronger developer is required, all the constituents may be increased in the same proportion. Nearly all the remarks made in connection with the sodium carbonate developer apply to the one just recorded.

When making up stock solutions of pyrogalllic acid, ferrous sulphate, or any easily oxidizable materials, it is a good plan to use the arrangement figured on page 65, whether a burette is employed or not. But, as every time a quantity of liquid is drawn off from the large containing vessel the same volume of air enters, it is necessary to put in an oxygen trap, as shown in fig. 5.

Either a small bottle can be used or a glass bulb intended for the purpose can be purchased at a chemical dealer's. The bottle or bulb contains an inch or so of strong pyrogalllic acid and soda in the

same proportions as used in the developer; this arrangement will last for a year or more without being renewed. If the oxygen trap, etc., is not available, do *not* put the whole stock into one *stoppered* bottle, as is generally recommended; but

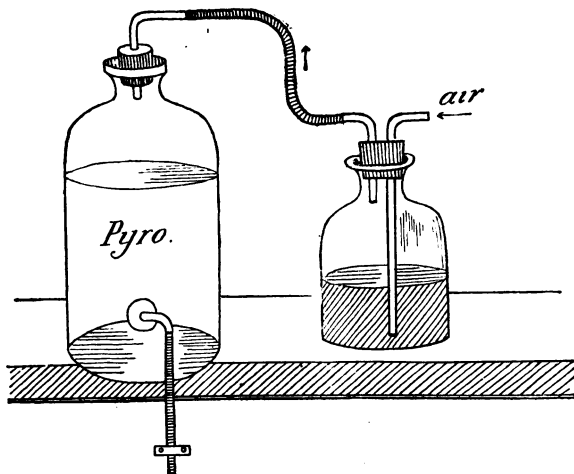


Fig. 5.

Fill a number of small corked bottles with the solution, cork them tightly, melt up some paraffin candle ends in an iron ladle or something of the kind, and dip the tops of the bottles in the melted paraffin to render them air-tight. Stock solution treated like this will keep indefinitely, and no preservative, such as citric acid, is required, as there is no large air space above the solution to make it go wrong.

Hydroquinone works more slowly than pyrogallie acid. For that reason there is less tendency to fog the plate during the prolonged development necessary for under-exposed plates, for which hydroquinone developer is very suitable. Although an excellent developer, there does not seem to be so much control over the plate as with pyrogallie acid.

The following is a good formula, giving a choice of either sodium hydrate or carbonate; the former is to be preferred. Except in cases of over-exposure, for which hydroquinone is not satisfactory, the bromide may be left out.

Hydroquinone,		. 8 gram,	. 4	grains.
Sodium sulphite (crystals),		3.5 ,,	. 16	,,
Citric acid,		. 05 ,,	. 1	1/2 ,,
Potassium bromide,		. 2 ,,	. 1	,,
{ Caustic soda,		. 4 ,,	. 2	,,
or				
{ Sodium carbonate (crystals),		3.0 ,,	. 15	,,
Water up to		100 c.c.,	. 1	oz.

Caustic soda is an inconvenient material to weigh out in small quantities, so that it will be better to make up a stock of 10% solution. The rest of the materials can be made up into a solution double the strength in the formula, thus:—

A. Hydroquinone,	. 16 grams,	. 160	grains.
Sodium sulphite,	. 70 ,,	. 1 1/2	ozs.
Citric acid,	. 1 ,,	. 20	grains.
Potassium bromide,	. 4 ,,	. 40	,,
Water up to	1000 c.c.,	. 20	ozs.

B. Caustic soda 10% solution,	80 c.c.,	1 $\frac{3}{4}$ ozs.
or		
Sodium carbonate 10% sol.,	600 „	13 $\frac{1}{2}$ „
Water up to	1000 „	20 „

For use take equal parts A and B. The same quantity of water may be added with advantage if the plate is not under-exposed. The strong alkali used in this developer is liable to cause frilling.

The best formula for the use of pyrocatechin is as follows:—

A. Pyrocatechin,	5 grams,	10 grains.
Sodium sulphite,	25 „	50 „
Water,	250 c.c.,	1 oz.
B. Sodium phosphate,	47 grams,	100 grains.
Caustic soda 10% sol.,	50 c.c.,	1 $\frac{1}{2}$ drams.
Water,	200 „	$\frac{3}{4}$ oz.

Use one part each of A and B and one part of water.

Eikonogen is a complicated organic sodium salt (see index). It is not a convenient developer to use, as it dissolves in water with difficulty and deteriorates rapidly when it has dissolved. Its action is very powerful, however, and many workers use it for developing snap-shots, lantern slides, and badly under-exposed plates. The following formula is recommended:—

A. Eikonogen,	5 grams,	24 grains.
Sodium sulphite,	20 „	96 „
Potassium bromide,	5 „	2 „
Water up to	300 c.c.,	3 ozs.

B. Sodium carbonate (crystals), 15 grams, 70 grains.

Water up to . . . 100 c.c., 1 oz.

For use take 3 of A to 1 of B immediately before developing. It is not advisable to make up more than is required for immediate use. For very under-exposed plates, the following may be used instead of B:—

Caustic soda 10% . . . 50 c.c., $\frac{1}{2}$ oz.

Water up to . . . 100 „ 1 „

Metol* possesses a marked effect in bringing out detail in under-exposed plates, and a mixture of this with hydroquinone is advantageous, because hydroquinone gives density, whilst metol brings out the detail.

Metol is an excellent developer, being preferred by many people to pyrogallie acid. The following is a good formula:—

Metol, 8 grams, . 4 grains.

Sodium sulphite (crystals), . 5.5 „ . 24 „

Sodium carbonate (crystals), 4.5 „ . 20 „

Potassium bromide, . . . 2 „ . 1 „

Water up to . . . 100 c.c., . 1 oz.

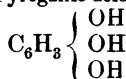
It is well to dissolve the metol first and then add the other constituents. Some people are very sensitive to the action of metol, which sets up violent inflammation in their hands.

Amidol is, chemically speaking, di-amido-phenol or pyrogallie acid in which two of the OH's are replaced by NH_2 . This last is derived from

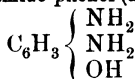
* For chemical formula see index.

ammonia, NH_3 , in the same way that OH is derived from water, OH_2 , and plays a very important part in organic chemistry.

Pyrogallic acid.



Di-amido-phenol (amidol).



It is a powerful reducing agent, and has the peculiarity of working without an alkali. The image comes up very quickly when using amidol, and care must be taken to leave the plate in the developer until it has attained sufficient density. Amidol dissolves more readily in a solution of sulphite than in water, and sulphite has an accelerating action with this developer. Amidol keeps very badly, and it is advisable to make up fresh solution for each batch of plates. It is not easy to restrain this developer, as bromides do not seem very effectual with it. The presence of a small quantity of bromide, however (say 1 drop of a 10% solution to each ounce of developer), prevents any tendency to fog.

Amidol,	5 grams .	2½ grains.
Sodium sulphite (crystals), 3·0 „	„	15 „
Water up to	100 c.c.	1 oz.

In case of under-exposure, add 1 c.c. to each 100 c.c., or 5 or 6 drops to each ounce of a 10% solution of sodium carbonate crystals, and the same quantity of potassium bromide.

Another material, called di-amido-resorcin, which

is very similar to amidol, has been proposed recently as a developer. The following is the formula recommended for use:—

Diamido-resorcin hydrochlorate,	. . .	1 part.
Sulphite of soda (crystals),	. . .	6 parts.
Water,	. . .	100 „

Paramido-phenol is hydroquinone in which one OH has been replaced by NH_2 .

Hydroquinone.	Paramido-phenol.
$\text{C}_6\text{H}_4 \begin{cases} \text{OH} \\ \text{OH} \end{cases}$	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} \\ \text{NH}_2 \end{cases}$

Its hydrochloride, or compound with hydrochloric acid ($\text{C}_6\text{H}_4\text{OH.NH}_2\text{HCl}$), is usually employed, and is sold in solution as “Rodinal,” which keeps excellently. Those who use it speak very highly of it as an all round developer, and the author has obtained good results with it in radiography. It is convenient to make up a strong solution, similar to rodinal, and dilute it when required.

Strong solution—

Paramido-phenol hydrochloride,	·5 grams,	25 grains.
Sodium sulphite,	. 9 „	1 oz.
Sodium carbonate (crystals),	. 9 „	1 „
Water up to	100 c.c.,	10 ozs.

For use, take—

Strong solution (Rodinal),	. . .	10 c.c.,	1 oz.
Potassium bromide 10% solution,	. 2 „	¼ „	
Water up to	100 „	10 „	

Glycin* can be made to give hard, sharp negatives.

* For chemical formula see index.

It is useful, therefore, in copying line drawings and similar subjects, and works well with kinematograph films. Glycin is rather insoluble by itself, but dissolves readily in alkali and sulphite. The following is a good formula:—

Glycin,		8 grams,		4 grains.
Sodium sulphite (crystals),	2	„		10 „
Sodium carbonate (crystals),	3	„		15 „
Water up to		100 c.c.,		1 oz.

For convenience, it may be made up four times this strength and diluted for use.

As regards the majority of these developers, it is difficult to say that one is better or worse than another. The best developer is undoubtedly the developer that suits the photographer's particular method of exposing, developing, and printing. The same *dictum* applies to the various formulæ, which must not be taken as absolute, but merely as general guides, to be varied according to circumstances.

Before closing the subject of development, attention must be paid for a few moments to the work of Hurter and Driffield, whose results are quite easy to understand. In a perfect negative, containing only black and white and no yellow stain, you have minute black spots on a transparent ground. Supposing you had a small plate, say one inch each way, and you divided it by cross lines into ten thousand equal squares, and then stopped up nine thousand so that no light could come through these particular squares, you would have something that would represent

roughly a photographic negative. If you put this in a printing frame against the light, only one-tenth of the light falling on the plate would come through. Supposing another similar plate were placed behind the first plate, it would pass one-tenth of the light that had filtered through the first plate, *i.e.*, one-tenth of one-tenth of the original light. The light coming through a third similar plate would be one-tenth of one-tenth of one-tenth of the original, and so on. That is to say, the light coming through each of the three plates would be $\frac{1}{10}$ th, $\frac{1}{100}$ th, $\frac{1}{1000}$ th, etc., of the original, or taking it the reverse way, the ratios between the lights would be 10, 100, 1000, etc. Now the logarithms of 10, 100, 1000, etc., are 1, 2, 3, and so on; so that the logarithm of the light stopped by one screen or one density is 1, by two screens, 2, by three screens, 3, etc. Supposing you want to photograph a scale of tones so graded that they are in the order 1, 2, 3, 4. A correct result will only be obtained if the printing values of the different parts of the negative are 1, 2, 3, 4; that is to say, "each density must be proportional to the logarithm of the light intensity that produced it." By experiment Hurter and Driffeld found that for every plate there was a particular exposure, within the limits of which this law held good; above and below these limits the ratios were false. More than this, they found that the gradation in a negative, developed with ferrous oxalate, could not be altered by any amount of development, supposing no fog

was introduced, but depended entirely on the exposure.

On this was based the H and D system of determining the sensitiveness of plates.

The plate receives exposures from a standard light graduated from $2\frac{1}{2}$, 5, 10, 20, 40 to 160 secs., the first portion of it, called the "fog strip," receiving no ex-

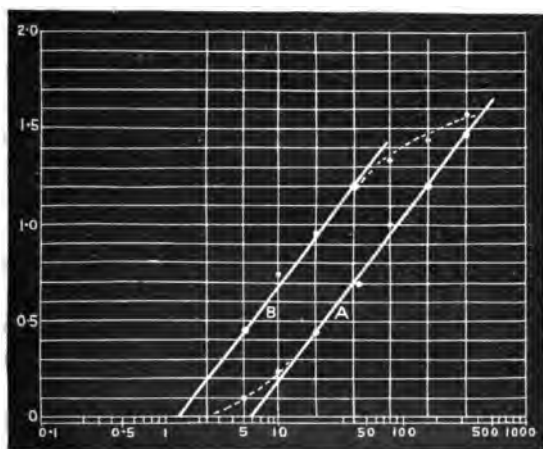


Fig. 6.—Speed readings of two plates—A, ordinary; B, rapid.

posure at all. This plate is developed in the standard developer for a standard time at a standard temperature (see p. 54), and the densities of the different strips are read on a photometer, and recorded in the manner shown above (fig. 6). The bottom line of the chart represents the logarithms of the exposures, and the upright line the densities read on the photo-

meter, the density of the fog strip being subtracted from each one. It will be noticed that several of the dots are in a straight line; this is the period of correct exposure. The straight line is prolonged to meet the base line, and the number read off, which gives the "inertia" of the plate, or the exposure required before the plate commences to register correctly. To obtain the H and D speed number, the figure where the straight line cuts the base is read off, and this divided into 34 gives the speed number required.

The important points brought out by Hurter and Driffield, in addition to the accurate method of determining the speed of plates, are first, that the gradation in a negative cannot be altered during development, unless fog or stain is introduced; and secondly, that pyro-ammonia is a very uncertain developer. Another point arises out of the former one, namely, that sensitiveness of the plate is as much a matter of the developer used as of the state of the emulsion itself, the speed number of the plate developed with pyro-soda being much higher than when developed with ferrous oxalate, and the speed number with metol, for instance, is higher still.

The Hurter and Driffield system, as has been pointed out, takes no account of the yellow stain produced by development with pyrogallie acid and other organic developers. Alfred Watkins and others have given considerable attention to this matter, and have shown that the "pyro-stain" has

an important influence on the printing value of the negative. This pyro-stain is something more than a mere stain, for if the silver be dissolved out of the plate with nitric acid, a faint yellow image remains. Light, oxidizing agents, tannin, and other agents cause gelatin to become insoluble. This is probably the explanation of the pyro-image. Various agents are present, such as the oxidized pyrogallie acid which resembles tannin in some respects, and the nascent compounds set free when the silver bromide is reduced, whilst the action of the light itself on the gelatin, and other little known causes, are at work to "tan" the gelatin. Wherever the gelatin becomes insoluble,—and this is most likely to happen where the chemical action of building up the silver image is taking place,—it fixes some of the highly coloured products of the oxidation of the pyrogallie acid or other phenolic developer.

As regards the "tanning" of the gelatin, or rendering it insoluble, formaldehyde (see p. 76) has a strong action, and is used to prevent plates frilling in hot weather. Plates washed with formaldehyde may be dried by means of heat, that could not be applied in the ordinary way without melting the gelatin. Formaldehyde is supplied commercially in 40 per cent. solution. This should be diluted as follows, and the plate should be immersed for ten minutes, being well washed afterwards:—

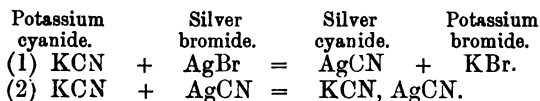
Formaldehyde (40% solution), . . .	1 part.
Water,	3 parts.

Following up the work of Schwartz and Mercklin, and of Hellheim, Messrs Lumière and Seyewitz have found that formaldehyde is not the only aldehyde capable of tanning gelatin. Aldehydes add to the reducing power of the developer, but only in the presence of sulphite. Acetone has a similar effect to aldehydes, and can be used advantageously to take the place of the alkali. With pyrogallie acid, development is effected rapidly; with hydroquinone, the development is not so rapid, but the results are as vigorous as with alkaline carbonates. Lumière and Seyewitz find that the addition of formaldehyde (formalin) to the developer causes strong staining of the film, with the exception of paramido-phenol (rodinal) and metol developers. The following are the formulæ recommended for development with acetone and sulphite in place of an alkali:—

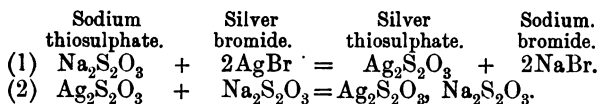
- | | | | |
|------------------------------|-------|-----------|------------|
| A. Pyrogallie acid, | . . . | 1 gram, | 5 grains. |
| Water, | . . . | 100 c.c., | 1 oz. |
| Sulphite of soda (crystals), | | 10 grams, | 50 grains. |
| Acetone, | . . . | 10 c.c., | 50 minims. |
|
B. Hydroquinone, | . . . | 3 grams, | 15 grains. |
| Sulphite of soda, | . . . | 20 " | 100 " |
| Acetone, | . . . | 10 c.c., | 50 minims. |
| Water | . . . | 100 " | 1 oz. |

When the plate has been developed to the right density, it is washed carefully under the tap, and allowed to soak for a few minutes in water; then it is fixed, *i.e.*, the unaltered silver salts are dissolved

out of the film, so as to leave no material sensitive to light on the plate. The principal, and practically the only, substances used for this purpose are potassium cyanide and sodium thiosulphate ("hypo."). The action of the two solvents is very similar: the first action of the cyanide is to form insoluble silver cyanide by double decomposition with the silver bromide, and then to make a double silver potassium cyanide, which is soluble in water.

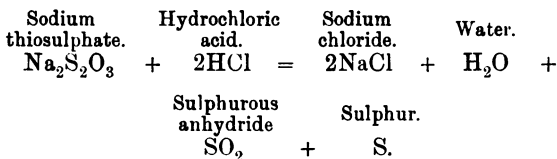


With thiosulphate, silver thiosulphate is first formed, and then a double soluble thiosulphate of silver and sodium.



The quantity of potassium cyanide to be used will be found under the development of wet plates (p. 41, which see). Of sodium thiosulphate, solutions varying from 40 to 10 of the crystals in 100 of water can be used, the former for negatives and the latter for prints. Haddon and Grundy have shown that 10 per cent. is the best strength for fixing prints on albumenized paper. It is well to employ a saturated solution of the salt (50 per cent.), and dilute just before starting development.

Acids decompose sodium thiosulphate into sulphurous anhydride (sulphurous acid gas, or burnt sulphur) and free sulphur. The reader should try the experiment of adding a little hydrochloric acid to a little solution of sodium thiosulphate. In a few moments he will be able to smell the burnt sulphur, and will see the liquid turn milky with free sulphur, thus—



Sulphurous acid has a very strong bleaching action, and the sulphur is liable to cause stains. Acid or alum, which contains free acid, should never be added to the fixing bath.

As soon as the fixing bath begins to work slowly, it should be thrown out and a fresh lot made up. Exposure to the air gradually oxidizes the thiosulphate and sets up decomposition. Old baths full of dirt and pyro-stains should not be used, as they are almost certain to bleach or discolour the negative or print.

As regards the washing of negatives free from thiosulphate after fixing, the reader is referred to page 14.

CHAPTER V.

REVERSAL.

IN one sense it is largely accidental that a "negative" is produced by the ordinary method of exposure and development. If a piece of paper be coated with ferric oxalate and exposed in the camera, the reduced image will be lighter than the unreduced—that is to say, a positive will be produced. If this be washed over with ferricyanide of potassium, the positive will be converted into a negative; if ferrocyanide had been used, the positive would have remained positive.

All chemical reactions are reversible, given proper conditions. In a mixture of substances such as exists in the film of a sensitive plate, where there is no outlet for the products of decomposition—the excess of bromide or other halogen set free on reduction in this case—a state of equilibrium is reached at a certain point. If decomposition is carried beyond this point, reversal sets in, which may go the whole way until the original compounds are re-formed.

This occurs in actual practice in photography. When a plate is over-exposed, the high lights are thin after development—*i.e.*, partial reversal has taken place. By great over-exposure, reversal can be carried to such an extent that a positive is obtained instead of a negative. This process is actually employed for copying negatives without going to the trouble of making a transparency and printing from that again. The resulting negative is reversed as regards right and left, which is a drawback if needed for ordinary photographic printing, though it is an advantage in many "process" applications.

The actual method of accomplishing this, due to T. Bolas, is as follows:—Soak a gelatino-bromide dry plate for five minutes in a 4 per cent. solution of bichromate of potassium, rinse once or twice, and then dip into a bath of equal parts of methylated spirit and water. Blot off the superfluous moisture and allow the plate to dry, all these operations being conducted in the dark room. Then expose the plate in a printing frame behind the original negative, and expose to direct sunlight for three or four minutes. On removal from the frame in the dark room a faint image will be seen on the plate, which is developed and fixed as usual. A chloride plate must not be used for this purpose, as the reduction of silver chloride cannot be reversed in the same way as silver bromide.

Several chemicals have the power of reversing a

plate in a similar manner to light. Sodium hypophosphite has this peculiarity. The organic substance thiosinamine and the organic salts known as thiocarbamides, when added to the developer, have this effect. Colonel J. Waterhouse recommends for this purpose the following developer :—

A. Lithium carbonate saturated			
solution,	. . .	100 c.c.,	. 1 oz.
Eikonogen,	. . .	1 gram,	. 5 grains.
Sodium sulphite,	. . .	1 „	. 5 „

Dissolve the two latter in the first just before using, and add a few drops of

B. Ammonium bromide,			
	. . .		1 part.
Thiocarbamide,	. . .		3 parts.
Dissolved in water (quantity not stated).			

“Solarization” is the word usually employed to denote the local reversals that sometimes occur on plates containing very strong contrasts. “Halation,” or the veiling or blurring of the edges of the high lights, such as the sky-lines of houses or the branches of trees taken against the light, is a species of partial reversal, generally attributed to reflection from the back of the plate. To prevent this it is usual to “back” the plate with some non-actinic medium, such as caramel and burnt sienna. The following formula, due to J. S. Teape, is a good one :—

Boil 1 lb. of white lump sugar in a saucepan large enough to hold twice the bulk, for one hour after it has

melted, stirring with a wooden rod the whole time. Allow the liquid to cool slightly, then add, in small quantities at a time, 4 ounces of *boiling* water, and stir between each addition.

Of this caramel take $1\frac{1}{2}$ ozs.

Saturated solution of gum tragacanth, 1 oz.

Powdered burnt sienna, 2 ozs.

Methylated spirit, 2 „

Add the spirit after the other ingredients are well mixed. Apply thinly to back of plate by dabbing with flat hog's-hair brush.

Instead of making the caramel from the sugar, it can be purchased; the dry powdered form is the best.

Some recent work of the author's seems to show that the caramel alone is sufficient to stop halation, and that the following formula is satisfactory:—

White starch or flour, 10 parts.

Caramel powder, 10 „

Sodium carbonate (crystals), 2 „

Methylated spirit, 25 „

Water, 75 „

Boil the water first; mix the starch into a thin paste with part of the water (cold) and pour into the boiling water; then add the caramel and, when thoroughly incorporated and cold, the spirit.

CHAPTER VI.

REDUCTION, INTENSIFICATION, ETC.

IF the image in the negative is too dense, it is sometimes necessary to reduce its intensity. Any perchloride, such as perchloride of iron, or similar salt, will have the effect of converting the silver of the image into chloride. This must be associated with an agent, such as thiosulphate of soda, which is capable of dissolving the silver chloride as it is produced, otherwise it would be difficult to know when the reduction had proceeded far enough. The method generally used in practice is that of Howard Farmer, in which a mixture of potassium ferricyanide and sodium thiosulphate is employed. The action is very simple, silver ferricyanide being produced, which dissolves in the thiosulphate. The reducing mixture should be made up in small quantities at a time, as the thiosulphate slowly reduces the ferricyanide, rendering the mixture useless. The negative should be soaked in water for ten minutes, and then be placed in a 12% solution of sodium thiosulphate to which a certain

quantity of 10% solution of potassium ferricyanide has been added; the amount can be regulated according to the rapidity of reducing action required. All the hypochlorites act on the silver image, and can be used to reduce its density.

Recently ammonium persulphate has come into use for reducing the density of negatives. Owing to the chemical reactions that take place in the upper layer of the film, the persulphate is said to act only on the deeper portions, so that the dense portions are reduced more in proportion than the half-tones. The persulphate must not be used in stronger solution than 5%; otherwise it acts upon the gelatin.

Intensification is very commonly employed, especially in wet plate negatives. All the methods employed have for their object the conversion of the particles of silver into some compound that will increase the printing value. With the exception of a few cases, the image is first bleached with mercuric chloride, which converts the black silver image into a white double silver-mercurous chloride. This must be washed carefully before proceeding to the next stage, and it is absolutely necessary to success in intensification that the film be thoroughly cleansed from "hypo." Mr Chapman Jones has done a great deal of valuable work on intensification.* He finds that the old

* See *Royal Photographic Society's Journal*, June 1897, and earlier issues.

method of treating the bleached plate with ferrous oxalate developer is by far the most reliable method. The plate is first of all treated to a bath of dilute hydrochloric acid containing one part in one hundred, and is then soaked in

Perchloride of mercury,	. . .	2 parts
Water,	. . .	100 „

until thoroughly bleached. After well washing, the plate is placed in a bath of ordinary ferrous oxalate developer (which see) until quite black, when it is again washed. If not sufficiently intensified, the whole operation may be repeated a second, and even a third time, the chemical effect being to form an amalgam of silver and mercury, which, through the protection afforded by the gelatin, is permanent.

A very common method is to treat the bleached plate with very dilute ammonia. The action in this case is very complicated, as the black intensified image consists principally of uncertain compounds of ammonia and mercury, the silver being largely dissolved out. Consequently, the effect on the plate is by no means uniform, the thinner parts being actually *reduced* by the solvent action just referred to. If employed, the ammonia solution should contain about ten drops of liquor ammonia .880 to the ounce.

Sulphite of soda can be used after bleaching with mercury, but the intensifying action is not very

strong or certain. The chemical effect is to reduce part of the silver and mercury to the metallic state, and to dissolve part as sulphites.

A mixture of potassium iodide and potassium cyanide is sometimes applied to the bleached plate. It is uncertain in its action, and changes take place on storing, as they do with plates blackened by ammonia. The same applies to a mixture of silver nitrate and potassium cyanide sometimes employed.

Wet plates are frequently intensified by silver nitrate mixed with an acid developer, such as pyrogalllic acid containing citric acid, the following being employed at the Bolt Court Process School :—

- | | | |
|----------------------|---------------|---------------|
| A. Silver nitrate, | . 22·8 grams, | . 200 grains. |
| Water distilled, | . 1000 c.c., | . 20 ozs. |
| B. Pyrogalllic acid, | . 11·4 grams, | . 100 grains. |
| Citric acid, | . 28·5 „, | . 250 „ |
| Water distilled, | . 1000 c.c., | . 20 ozs. |

Ferricyanides of uranium and lead are occasionally used, the action being to form an insoluble ferrocyanide. It is therefore very important that in making the solution the crystal of ferricyanide of potassium be washed free from any adhering ferrocyanide. The uranium ferrocyanide is red in colour, and is very opaque to the rays causing photographic action, so that care must be taken not to over-intensify. The lead ferrocyanide is white, and must be treated with ammonium sulphide, which turns it

into black sulphide of lead. Instead of the ferricyanides of lead or uranium, a mixture of potassium ferricyanide and lead or uranium nitrate is used.

Lead Intensifier.

Lead nitrate,	4 grams,	20 grains.
Potassium ferricyanide,	6 „	30 „
Acetic acid (glacial),	2 c.c.,	10 minims.
Distilled water up to	100 „	1 oz.

Uranium Intensifier.

Uranium nitrate,	1 gram,	5 grains.
Potassium ferricyanide,	1 „	5 „
Acetic acid (glacial),	2 grams,	10 „
Distilled water up to	100 c.c.,	1 oz.

Mr Charles W. Gamble has pointed out an interesting point in connection with intensification of half-tone negatives by lead. If the mixture of lead and silver ferricyanides is treated with fresh ammonium sulphide, the dots in the negative come out sharp and black, but if the ammonium sulphide has been made up several days, each dot is surrounded by a grey margin instead of being sharp. The explanation of this is, that, on exposure to the air, ammonium sulphide is oxidized to a mixture of thiosulphate and polysulphides which have a solvent action on the silver, which is first dissolved and then re-precipitated as a blurred margin round the dot.

CHAPTER VII.

PRINTING IN SILVER.

FROM the short account given on page 36, the reader will have learnt something about the photo-chlorides of silver. These intermediate compounds between ordinary silver chloride and metallic silver are of most varied colours, ranging from white through shades of red and purple to black. They are permanent in the dark, but are altered by light. Besides these coloured photo-chlorides and other photo-salts of silver, there are several coloured varieties of metallic silver, which in this state more resembles a colloid substance (see p. 113), and possesses the remarkable property of dissolving in water. In addition to the ordinary white form of metallic silver, there seem to be at least four other modifications. The first, which we may call A, is soluble, forming a deep red solution in water. When concentrated, or if nitrate of ammonium is added to the solution, it forms a precipitate, which may be either matt black, blue or green, whilst moist. As soon as it is dry, however, it acquires a brilliant metallic surface, having a

bluish-green tint. Modification B is insoluble, and is produced from the foregoing; it is dark reddish-brown when moist, but resembles A when dry. The third form, C, is of a dark bronze hue when moist, but like burnished gold when dry. No soluble modification of this exists, but a copper-coloured variety is formed under certain conditions. All the varieties have the remarkable property of drying with their particles in optical contact, producing perfect mirrors if spread out on paper and allowed to dry. Unfortunately, like the photo-chlorides, these forms of metallic silver are affected by light; A and B become brown after some hours, and the coppery modification of C becomes bright yellow. In spite of this, several occasions can be imagined on which they would be serviceable for making a large mirror for immediate use in the studio, or where a large reflecting surface is required. C has the property of changing into ordinary silver of great beauty in presence of moisture, and immediately, on being subjected to friction in any part, the action spreading to the rest of the film. The reader has probably seen a good many of these photo-chlorides and varieties of metallic silver in the ordinary silver printing papers after exposure behind the negative.

The old process of sensitizing albumen paper with silver nitrate is still the most largely used of any printing process in spite of numerous drawbacks. In preparing the paper on a large scale, the eggs

are broken separately, the whites separated from the yolks and run into drums. This albumen is then run into churns driven by steam and "frothed," being allowed to stand until quite limpid, when it is decanted off from the embryos and stringy portions of the white of egg, and run into tall glass jars to ferment. After this it is filtered and again treated to the frothing process and allowed to settle, the stringy portions being now finally removed. Ammonium chloride is added to the albumen, and Rives or Saxe paper is coated by floating the sheets on the surface of the liquid. The paper is hung up to drain, stored for some time and re-albumenized, being hung up to drain the reverse way. This procedure equalizes the quantity of albumen on the surface.

From this description of work on the large scale, the reader will see how to proceed in the small way if ever he finds it necessary to do so, the following quantities of materials being used, and a whisk being employed instead of a churn:—

Albumen,	6	ozs.
Ammonium chloride,	60	grams.
Rectified spirit,	96	minims.
Distilled water,	1 $\frac{3}{4}$	ozs.

The paper is sensitized just before use by floating on a solution of silver nitrate containing 50 grs. to the oz., or 10 grams in 100 c.c.

The action of the sensitizing bath is to convert

the silver nitrate into chloride, which is entangled in the albumen by interaction with the ammonium chloride. Besides this, however, the silver nitrate has an important action on the albumen, forming an albumenate of silver, which is insoluble in water, so that the albumen does not dissolve off the paper. Consequently, the stronger the sensitizing bath, the longer will the paper have to be floated, as the silver nitrate penetrates more slowly through the insoluble albumenate.

In printing on this paper the action is probably very complicated, as the albumenate of silver takes part in the reduction as well as the chloride. The ready sensitized paper, used so largely by amateurs, contains citric acid in addition to the other constituents, which still further complicates matters.

When printed, the paper is washed in water containing one part of common salt in 40, and toned with gold or other more or less permanent reducible metal, in order to counteract the objectionable red tones of the silver print. In washing the print before toning, the reason that the water turns milky is that the soluble silver salts react with the salt in the water to form chloride.

Of the numerous toning baths, the acetate is that most usually employed. The gold chloride generally purchased is a double chloride of gold and sodium, and is frequently acid. It is important, therefore, to neutralize the gold chloride solution by shaking it up with a little powdered chalk. For use it is

convenient to dissolve the contents of the 15-grain tube in $1\frac{1}{4}$ ounces of water, making approximately 1 grain to 1 dram or a 2 per cent. solution; or if dissolved in 50 c.c. of water, a practically 2 per cent. solution of the commercial salt, or a 1 per cent. solution of gold, is obtained. The following Table shows a few of the various formulæ recommended by different workers for toning sensitized paper with gold.

TABLE VIII.—GOLD TONING BATHS.

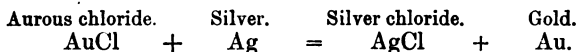
Each to be made up to 10 ounces with water.

Substances.	I.	II.	III.	IV.	V.	VI.	VII.
Gold chloride (commercial), 2% solution, . .	2 drams	2 drams	2 drams	2 drams	1 dram	1 dram	2 drams
Acetate of soda,	90 grains	..	48 grains	..	..	..	..
Borax,	..	..	..	96 grains	..	..	..
Bicarbonate of soda, . .	..	..	4 grains	..	30 grains	..	..
Carbonate (washing soda),	..	10 grains	..	..	..	..	..
Phosphate of soda, . .	..	..	..	..	..	20 grains	..
Tungstate of soda, . .	..	..	..	..	..	..	40 grains

When toning has reached a stage where the blue of the gold neutralizes the objectionable red and orange tones of the original, the print is fixed in a 10 per cent. (2 ounces to the pint) solution of sodium thiosulphate. It is even more important with prints than with negatives to always keep the fixing bath in perfect condition. The least trace of acid means the presence of free sulphur (see p. 77). Under

these conditions, sulphur combines with the silver, forming silver sulphide, and the toning is due to the sulphur instead of to the gold; such prints fade very rapidly, and the whites soon turn yellow. For this reason combined toning and fixing baths cannot be too strongly condemned. Consequently, the fixing bath should be made alkaline by the addition of ammonia, or, better, bicarbonate of soda in the proportion of 5 grains to each ounce of "hypo." Always test with litmus-paper before use; if acid, *i.e.*, if the litmus-paper turns red, add more bicarbonate. Toning baths should be made alkaline with bicarbonate in the same way, if on the acid side, as it is essential that the bath be alkaline. After toning, it is well to immerse the prints in salt and water before fixing. They may be left there until all the batch has been toned, so as to avoid contamination of the fingers with the fixing bath whilst toning is in progress.

The chemistry of the toning process is as follows: In the alkaline solution the gold chloride is reduced first of all from auric chloride (AuCl_3) to aurous chloride (AuCl); then an atom of gold is deposited, an atom of silver taking its place, thus,



From this it is clear that other metals can be used for toning instead of gold. With a platinum toning bath, for instance, platinum is deposited in the place of the silver, and with a lead toning bath,

lead is exchanged for the silver in the print. The following platinum toning bath is recommended by Liesegang :—

Potassium chloroplatinite, .	.1 gram,	$\frac{1}{2}$ grain.
Nitric acid,	.5 c.c., .	2 minims.
Water,	100 „	1 oz.

Gelatino-chloride and collodio-chloride papers are emulsions of silver chloride and an organic salt with gelatin in the one case and with collodion in the other. These papers are generally known as “printing-out” papers.

W. K. Burton's formula for gelatino-chloride emulsions is as follows:—

A. Ammonium chloride,	3.5 grams, .	53 grains.
Gelatin,	27 „	420 „
Distilled water,	850 c.c., .	30 ozs.

Soak the gelatin and ammonia chloride in the water for an hour and dissolve in a water-bath; then add

Silver nitrate,	9.7 grams, .	150 grains.
Distilled water,	14 c.c., .	$\frac{1}{2}$ oz.
B. Sodium citrate,	2 grams, .	30 grains.
Gelatin,	6.3 „	100 „
Distilled water,	100 c.c., .	$3\frac{1}{2}$ ozs.

Allow to soak for an hour and dissolve in the water-bath; then add

Silver nitrate,	3 grams, .	45 grains.
Citric acid,	5 „	80 „
Distilled water,	14 c.c., .	$\frac{1}{2}$ oz.

Mix A and B; wash as directed in dry-plate emulsions, and after keeping for three or four days, coat the paper by floating.

Geldmacher's formula for collodio-chloride emulsion is as follows:—

A. Pyroxylin,	22.75 grams,	6½ drams.
Ether (not methylated),	425 c.c., .	15 ozs.
Alcohol (not methylated),	425 „ .	15 „
Castor oil,	3.5 „ .	1 dram.
B. Silver nitrate,	20 grams,	308 grains.
Distilled water,	21.5 c.c., .	6 drams.
Alcohol (not methylated),	42.5 „ .	1½ ozs.
C. Citric acid,	5 grams,	75 grains.
Alcohol,	70 c.c., .	2½ ozs.
D. Strontium chloride,	5 grams,	75 grains.
Alcohol,	70 c.c., .	2½ ozs.

Mix C and D and add to A, shaking vigorously. In the dark room, add B to the mixture in small portions at a time, shaking constantly. The emulsion is ready for use after standing for an hour.

Alpha paper is essentially a gelatin emulsion of silver citrate. The following is Wellington's formula:—

A. Silver nitrate,	53.5 grams,	825 grains.
Citric acid,	53.5 „ .	825 „
Distilled water,	142 c.c., .	5 ozs.
B. Sodium chloride,	10.7 grams,	165 grains.
Potassium bromide,	21.4 „ .	330 „
Citric acid,	53.5 „ .	825 „
Gelatin,	21.4 „ .	330 „
Distilled water,	142 c.c., .	5 ozs.

Both solutions are to be heated to 66° C. A is then added to B, and 1600 grains (10·4 grms.) of gelatin, previously swollen and melted, is added to the mixture, which is run into a dish and allowed to set. It is then broken up, washed and re-melted before coating the paper, which is best developed with the hydroquinone formula given below (p. 99) and toned.

As regards toning, the collodio- and gelatino-chloride papers may be treated alike. The same baths may be used as for ordinary sensitized paper, but these papers work better in a bath composed of ammonium sulphocyanide and gold chloride than in any other. The quantity of sulphocyanide may vary considerably, but as it has a tendency to dissolve gelatin, it is not advisable to use more than is recommended in the formula. These printing-out papers require to be toned somewhat more deeply than ordinary sensitized paper. The gelatin paper should not be touched with the fingers, as the gelatin is apt to soften with the warmth and retain the marks; for the same reason, all solutions should be kept cold. To prevent uneven toning, it is well to give the prints a thorough washing, preferably in salt and water (see p. 87); before toning. The following bath can be recommended:—

Gold chloride (2% solution),	6 c.c.,	1 dram.
Ammonium sulphocyanide (10% solution),	30 „	5 drams.
Water,	100 „	16 ozs.

Ammonium sulphocyanide is very deliquescent, and should be dissolved in water at once to form a 10% solution. In making up the bath, always mix the sulphocyanide with the water first, and then add the solution of gold chloride.

In toning, it should always be borne in mind that the number of prints that can be toned with a given quantity of gold depends quite as much upon the nature of the prints as upon their size. A dark print with heavy shadows may require three or four times as much gold as a light print of, say, a cloud effect. It is important, when economy of gold is desired, to trim the prints before toning.

The following formula has been strongly recommended by printers:—

Gold chloride (2% solution),	1.5 c.c.,	. 3 drams.
Ammonium sulphocyanide		
(10% solution),	20 „	. 2 ozs.
Sodium thiosulphate,	1 gram,	. 5 grains.
Water up to	100 c.c.,	. 10 ozs.

Numerous other formulæ are in existence, and will be found in the various year books and other books of reference, but exigencies of space forbid their inclusion here.

Some photographers use and recommend the combined toning and fixing baths. These may be all very well for routine work in careful and experienced hands, but they are wrong in principle, and the least carelessness may produce disaster. The author never uses them himself, and gives the

following formula, which is due to Dr Liesegang, under protest, so to speak:—

Ammonium sulphocyanide		
(10% solution), . . .	10 c.c.,	10 drams.
Common salt, . . .	4 grams,	240 grains.
Alum, . . .	2 „	120 „
Sodium thiosulphate (hypo.),	15 „	2 ozs.
Distilled water up to . .	100 c.c.,	12 „

To 60 parts of this solution, add 7 parts of a 2% solution of gold chloride, diluted with an equal bulk of water. When the mixture has been made, add 40 parts of old, used, combined bath.

Printing-out papers can be developed after a short exposure, and can then be toned and fixed in the usual way. Only a faint image is required to start with, and it is advisable not to print beyond the point where the details just begin to show in the half-tones. It is well to follow the excellent suggestion of Mr Wilson of the Paget Prize Plate Co. and immerse the prints in a 10% solution of potassium bromide before developing, thus changing the silver chloride into silver bromide. After soaking in this solution for from 10 to 20 minutes, passing a clean camel-hair brush over the surface of the paper to ensure the absence of bubbles, the paper should be thoroughly washed for about 10 minutes in running water to remove excess of potassium bromide, which would render the development too slow. Then develop with the following:—

A. Hydroquinone,	2 grams,	10 grains.
Sodium sulphite,	2 „	10 „
Sulphurous acid,	1 c.c.,	5 minims.
Water up to	100 „	1 oz.

B. Sodium carbonate (washing soda),	5 grams,	$\frac{1}{2}$ oz.
Water up to	100 c.c.,	10 ozs.

For use, take one part each of A and B, and one part of water.

The papers can be toned with platinum; for formula see p. 94.

Bromide paper is coated with a gelatino-bromide of silver emulsion similar to that used for dry plates, but generally much less rapid. The following is Dr Eder's formula for an emulsion suitable for coating paper:—

A. Ammonium bromide,	20 parts.
Gelatin,	50–80 „
Distilled water,	400 „

Soak the gelatin in the water for 12 hours, then dissolve in the water-bath at 50–60° C., and add the bromide. Take the emulsion into the dark room, and add, with constant shaking,

Silver nitrate,	30 parts.
Distilled water,	400 „

After standing for about an hour, pour out into a dish to set, squeeze through muslin, and wash in the manner described on page 52. The above formula gives black tones. If brown tones are required,

replace two parts of the ammonium bromide by two parts of potassium iodide.

Bromide paper may be developed with ferrous oxalate or with most of the dry plate developers, except pyrogallie acid. The author much prefers ferrous oxalate. The following is a good formula :—

- | | | |
|-------------------------------|-----------|---------------|
| A. Neutral oxalate of potash, | 23 grams, | 1 lb. avoird. |
| Distilled or boiled water, | 100 c.c., | 3½ pints. |
| B. Ferrous sulphate, . . . | 30 grams, | 1 lb. avoird. |
| Sulphuric acid, . . . | 5 c.c., | 15 minims. |
| Distilled or boiled water, | 100 „, | 54 ozs. |

For use, add one part of B to six parts of A, not the reverse, or a precipitate of ferrous oxalate would be formed. A few drops of 10% potassium bromide solution may be added as a restrainer.

If, after development, the prints were to be put direct into water, a precipitate of ferric hydrate would be formed in the paper. To avoid this, the paper is placed in dilute sulphuric acid (say ½ oz. in a pint, or 25 c.c. in 1000 c.c.) which dissolves out any iron from the paper.

As regards development with agents other than ferrous oxalate, the combinations that can be made are almost unlimited. For practical purposes, any of the formulæ used for dry plate development may be employed, but the strength must be only one-third of that given in the formulæ for dry plates. The proportion of sulphite in each ounce or 100 c.c. of developer, however, may remain the same or be

only slightly reduced, so as to ensure absence of stain.

Bromide prints are frequently toned with platinum or uranium salts. In the former case, the platinum replaces the silver to a greater or less extent. Uranium, although it changes the tone to a reddish-brown, acts principally as an intensifier, and can be applied beneficially to weak prints. It is important that every trace of "hypo." be removed by thorough soaking, otherwise toning will be uneven. Selle's formula for uranium toning is essentially as follows:

Uranium nitrate, . . .	5 gram,	2½ grains.
Potassium ferricyanide, . .	5 " ,	2½ " ,
Acetic acid (glacial); . .	10 grams,	¾ dram.
Water up to . . .	100 c.c.,	1 oz.

After toning, the print should be washed in dilute acetic acid (say 1 to 30) for twenty minutes or longer.

CHAPTER VIII.

PRINTING IN SALTS OF IRON.

PRACTICALLY the whole of the processes for printing in salts of iron depend upon the fact that ferric salts are reduced to the ferrous state by the action of light, ferric oxalate, $\text{Fe}'''_2(\text{C}_2\text{O}_4)_3$, becoming ferrous oxalate, $\text{Fe}''\text{C}_2\text{O}_4$. Potassium ferricyanide converts the reduced salt into insoluble Prussian blue, the unreduced ferric salt being nearly colourless and soluble. If *ferrocyanide* of potassium be used as a developer instead of *ferricyanide*, the reduced portions remain colourless, whilst the unreduced parts are turned blue.

The paper usually employed for reproducing engineering plans, and for making blue prints from negatives, is coated with a mixture of ammonio-ferrous citrate, better known as ammonio-citrate or citrate of iron, potassium ferricyanide and gum arabic in water. The process was first employed by

Sir John Herschell in 1842. The following is Rockwood's formula :—

- A. Potassium ferricyanide, . 10 grams, . 1 oz.
Water, 100 c.c., . 10 ozs.
- B. Ammonio-citrate of iron, . 30 grams, . 3 „
Gum arabic, 5 „ . ½ oz.
Water, 100 c.c., . 10 ozs.

Equal parts of A and B to be taken, and after standing for a few minutes until quite clear, the paper should be coated by means of a stiff brush. The paper should be dried quickly and kept dry. It is fixed by washing in water until the whites are quite clear. If over-printed, a little carbonate of soda may be added to the water. If under-printed, fuller density may be obtained by adding a little ferric salt to the first wash water and allowing it to remain until sufficient depth is obtained. This is the same principle as re-developing a gelatino-bromide plate. Spots can be bleached by a weak solution of potassium oxalate.

This paper can be toned with various substances. Strong tea containing a little sodium carbonate changes the blue to black, the iron forming an ink with the tannin. The colour can be altered by different reagents, sulphocyanide turning it red, and so on.

If the paper be coated with the iron solution (B) only, without the ferricyanide, it can be developed with this solution, or with gold chloride.

The process of making a paper for subsequent

development with ferrocyanide of potassium, whereby the whites of the negative come out white, is as follows, using Pizzighelli's formula :—

- | | | | | |
|-----------------------------|-----------|-----------|-----------|--------|
| A. Gum arabic, | | 20 grams, | | 2 ozs. |
| Water, | | 100 c.c., | | 10 „ |
| B. Ammonio-citrate of iron, | | 50 grams, | | 5 „ |
| Water, | | 100 c.c., | | 10 „ |
| C. Ferric chloride, | | 50 grams, | | 5 „ |
| Water, | | 100 c.c., | | 10 „ |

For use, add 20 parts of A to 8 parts of B, and the whole to 5 parts of C. Allow to stand until clear and then coat the paper. As the reduced ferrous is lighter than the ferric salt, the image appears lighter than the background.

Develop with—

- | | | | | |
|-------------------------|-----------|-----------|-----------|--------|
| Potassium ferrocyanide, | | 20 grams, | | 2 ozs. |
| Water, | | 100 „ | | 10 „ |

Paste the developer on the surface of the print with a brush; as soon as dark enough, wash, and fix in a 10% solution of hydrochloric acid until the whites show clear.

Those who want further information about ferric printing processes will find all they require in an excellent little work by G. E. Brown, F.I.C., entitled "Ferric and Heliographic Processes."

CHAPTER IX.

PRINTING IN PLATINUM.

PLATINUM printing is not a direct process; it is really an iron printing process, but instead of bringing out the reduced ferrous image with ferricyanide, a platinum salt is used, the platinum being reduced by the ferrous image to form a permanent print. The platinum salt can be incorporated in the sensitizing solution that is applied to the paper, as in the cold process, or the iron image can be obtained first by printing on paper coated by ferrous oxalate, and treating this afterwards with a solution containing platinum, as in the hot-bath process. Platinic chloride, PtCl_4 , can be used, but the effect is not good, as the salt has to be reduced such a long way, so that the lower or platinous chloride gives better results. This salt is nearly insoluble in water, but a double chloride of platinum and potassium is very soluble, so that the latter or potassium chloroplatinite, as it is generally called, is the actual salt employed.

By the addition of mercuric or palladium salts to the sensitizing solution, "sepia-" toned images

can be secured. The sepia tone does not appear to be due to any admixture of a mercury or palladium compound, but, as V. Hubl has shown, to a peculiar condition of the platinum itself.

W. Willis and Captain Pizzighelli are the two best-known workers on platinum printing, the hot-bath process of the former inventor being still the most reliable printing method, and that most generally used. Rives paper, No. 74, is sized with arrowroot and gelatin, in some such proportion as the following:—

Arrowroot,	500 grains.
Nelson's gelatin,	180 „
Alum,	110 „
Water up to	120 ozs.

The gelatin is allowed to swell and then dissolved at about 80° F.; the arrowroot, being made into a thin cream with a little of the cold water, is then poured in. The paper is sized on this for about three minutes by floating, and after being hung up to dry, is sensitized by coating with the following solution:—

I. Ferric oxalate, . . . 24 grams, . . 120 grains.
(Carefully prepared and kept away from the light, so as to ensure absence of ferrous salt.)

Oxalic acid,	1½ grams, . .	8 grains.
Distilled water,	100 c.c., . .	1 oz.

II. Potassium chloro-platinite solution } 24 parts.
(80 grs. to 1 oz. of water) . . . }
No. 1 solution, 22 „
Distilled water, 4 „

The addition of a few drops of 1% solution of potassium chlorate produces contrast, and should be used in case of a weak negative, or where a brilliant print is desired.

Coat the paper in a room heated to 70° F., the atmosphere being kept moist. The paper should be allowed to get surface dry, and should then be dried completely on an iron plate in front of a fire, taking care not to overheat. To keep the paper dry, it should be stored in a tin having a lid at each end, the bottom lid containing asbestos fibre soaked in strong calcium chloride, and dried bone dry by heating on an iron plate. A perforated zinc grating should cover the calcium chloride and asbestos to prevent any contact with the paper.

It is important to keep the paper as dry as possible whilst printing, and for this purpose sheets of india-rubber are placed behind the paper in the printing frames. Printing is allowed to continue until a faint iron image is visible, when it is developed with a solution of oxalate of potash at a temperature not lower than 100° F. The solution of oxalate of potash contains—

Potassium oxalate (neutral),	.	.	.	16 parts.
Water,	.	.	.	60 „

Hard negatives or under-exposed prints require a hotter oxalate bath, as it tends to soften and flatten the detail.

When developed sufficiently, the prints are fixed without washing in a bath containing—

Hydrochloric acid,	1 part.
Water,	60 parts.

The solution is poured away after a few minutes, and fresh poured on, this being again repeated. The object is to dissolve out every trace of iron and unreduced platinum salt. The paper must be washed to remove the acid.

Paper is made for developing in the cold, but this paper gives very brilliant results in the hot bath.

By adding mercuric or cupric chloride to the developing solution, a sepia tone is produced. Various substances can be used to tone or intensify platinum prints, but with the exception of catechu, they are not to be recommended. The toning-bath is prepared by boiling 7 grams of powdered Bombay catechu with 150 c.c. of water for ten minutes, cooling, adding 30 c.c. of alcohol, and filtering. Of this concentrated solution 5 c.c. are taken and made up to 500 c.c. at 60° F. As the catechu-tannic acid in the catechu combines to form an inky compound with iron, it is important that every trace of the latter be removed from the paper before toning.

CHAPTER X.

THE BICHROMATE PRINTING PROCESSES.

ALL that can be told about the chemistry of the bichromate processes, so far as it is known, can be said in a very few words, the subsequent applications of this knowledge being purely mechanical. There are two chromates of potassium, the normal yellow chromate (K_2CrO_4), and the acid orange chromate ($K_2Cr_2O_7$). When the latter is mixed with a colloid organic substance (see p. 114) and exposed to light under a negative, two important changes are noticed: the organic matter is rendered comparatively insoluble where the light has acted, and the material has lost its power of absorbing water and becoming sticky, or "tacky." On these facts the whole of the bichromate processes depend.

In the carbon process, carbon, Bartolozzi red, or some other colouring matter is incorporated with gelatin, and made into thin sheets of "tissue," which, about twelve hours before use, are sensitized by immersing in a 5 per cent. solution of potassium bichromate for three minutes in winter and two in

summer, at 60° F. They are then hung up to dry in the dark. The exposure is made under a negative, the time required being judged by means of an actinometer. After exposure, the tissue is transferred from its own paper to another paper prepared specially beforehand by coating with—

Nelson's No. 1 gelatin,		$\frac{1}{2}$ oz.
Water,		10 ozs.

Allow the gelatin to soak for an hour in the cold water, and then dissolve in a water-bath. When dissolved, stir in half a dram of formalin. Brush well over the surface of the paper, and allow to dry. The object of this is to make sure that the tissue will stick fast when squeegeed on to the paper.

The transfer paper is soaked in water for a time, which varies according to the thickness of the paper. The tissue is then placed in the same water with the prepared paper, and when the tissue begins to flatten, the two are lifted from the water together, being then squeegeed into close contact by means of a flat squeegee. After being pressed between blotting boards, the whole is immersed in hot water at about 110° F. As soon as the gelatin begins to soften round the edges, the original supporting paper is removed.

The back of the sensitive gelatin film is now uppermost, the surface on which the light has fallen being beneath. Where the light has acted

strongly, the gelatin is insoluble nearly right through, but in the parts corresponding to the black parts of the negative only a thin film is insoluble. By washing the film from the back, which is now uppermost, the soluble portions will be washed away, leaving a sort of raised map, the hills corresponding to the light parts of the negative, and the dales to the dark portions. Where the gelatin becomes insoluble, it entangles and fixes the colouring matter, so that a print in monochrome with all the gradations of the original is produced.

The method just described is that of single transfer, the right and left of the original subject being reversed. In some cases this is objectionable, so the tissue is developed on a temporary support, consisting generally of opal glass, coated with the following:—

Pure bee's wax,	.	.	.	.	2 drams
Yellow resin,	.	.	.	.	6 „
Turpentine,	.	.	.	.	1 pint,

any excess being removed by polishing with a cloth; paper coated with a film of partially soluble gelatin to be used as a final support. Before use, a sheet is soaked for half-an-hour in a 2 per cent. solution of alum, and then placed in water with the supported tissue, which should be transferred in the manner described under single transfer.

In both cases the development should be carried out with warm water, the temperature of which can be varied according to the correctness of the

exposure, higher temperature being employed for under-exposed prints. After development, the prints should receive a final wash with cold water, and should then be soaked in a 5 per cent. solution of alum until all bichromate stain has been removed, when a final rinse with cold water is given. The development should be carried out as soon as possible after printing, as the action once started by the light continues automatically in the dark. It is advisable to "safe edge" the print before exposing, by protecting the margin of the negative from the light by means of black paper. All who are interested in carbon printing should read J. A. Sinclair's excellent monograph, which appeared, together with other valuable and interesting papers on the bichromate processes, in the *Journal of the Royal Photographic Society* for May 1896, the set of papers being subsequently published by Dawbarn & Ward, Ltd.

A very beautiful process for carbon printing without transfer has been revived recently, and is known as the Artigue or bichromate gum process, an account of which will be found in Mr Sinclair's paper. Instead of gelatin, a warm black pigment is worked up with gum, and coated on paper. This is sensitized in a 2 per cent. solution of bichromate of potash, and exposed under the negative without a "safe edge," an actinometer being employed as in the ordinary carbon process. In development, the paper is first treated with warm water, and then

with a mixture of warm water and fine sawdust. After development is complete, the paper is soaked in a 5 per cent. solution of alum, and then washed in cold water.

The Gum-Bichromate process, which has been the subject of so much controversy, is somewhat similar to the Artigue process.

In the half-tone process of reproducing photographs and tone drawings, a copper, or sometimes a zinc, plate receives a coating of gelatin or other colloid, which is sensitized with bichromate. This is exposed under a negative made from the original through a cross line or other screen which breaks up the tones into dots. After printing, the plate is developed by washing, and etched with ferric chloride or an acid. There are various modifications of this process, all depending on the action of light causing the gelatin to become insoluble. For details of these processes other works should be consulted.

In collotype, advantage is taken of the fact, previously mentioned, that when bichromatized gelatin is acted upon by light, it loses its tendency to absorb water and become tacky. After printing under the negative, the sheet of gelatin is fixed on the press and kept moist. Where the light has acted, the surface takes the ink in proportion to the amount of light that has fallen upon it. Several other processes depend upon this selective action of the gelatin as regards greasy ink.

Glue, fish-glue, size, and isinglass are all forms of gelatin. They are colloids—*i.e.*, they will absorb water to an indefinite extent, but do not pass through animal membranes, such as bladder, as a solution of salt, sugar, or other crystalloid substances would do. For photographic purposes, gelatin should contain little ash—not more than about 3 per cent.—should take up from five to ten times its weight of water when soaked in the cold, and sufficient to dissolve it on warming to 85° F.

In the common line-engraving process, asphaltum is generally used as the sensitive substance. This asphaltum or bitumen is obtained from deposits of pitch in different parts of the world. It has a peculiar smell, and resembles the heavier portion of gas tar. It is partly soluble in alcohol and ether, more so in benzene and essential oils, and dissolves completely in chloroform, carbon bisulphide, and mineral oils. Caustic alkalies dissolve it; hot sulphuric acid dissolves and decomposes it, but nitric acid is without action upon it. Asphaltum is sensitive to light, and is obtained in best condition by exhausting with ether, the insoluble portion being dissolved in benzene. A plate is coated with a varnish of this material, and exposed to light under a negative or transparency, being developed with a mixture of benzene and turpentine, which dissolves off the bitumen that has not been rendered insoluble by light. The plate is then etched and treated in various ways.

CHAPTER XI.

ORTHOCHROMATISM.

LIGHT does not affect an ordinary gelatino-bromide emulsion in the same manner as it does the eye. The latter is most sensitive to the yellow of the spectrum in the neighbourhood of the sodium or D line, but the violet and ultra-violet part of the spectrum has the greatest effect on a gelatino-bromide film. To remedy this defect, yellow or yellow-orange light-filters are introduced, either in front of the lens, or between the lens and the plate. The effect of this is to cut off the violet end of the spectrum to a greater or less extent. The author has investigated a large number of these filters, and has found considerable variations in their absorptive powers. As a general rule, the gelatin or collodion filters should be avoided, as the colouring matter in this form has a great tendency to fade. The filter should consist of a cell filled with a standard coloured solution, which should be renewed from time to time. The question of what filter to employ is a very difficult one, as the action depends

so largely on the strength of the light. It is unfortunate that no standard light-filters have yet been fixed upon for iso-chromatic work, although several dry-plate makers have introduced light-filters which are eminently satisfactory.

In addition to this means of modifying the light before reaching the plate, it has been found that certain organic dyes have an important influence on the absorptive power of the silver salt for the different parts of the spectrum. The undyed gelatino-bromide plate is most affected by the blue rays, the action of the green and red on the plate being very small in comparison. In a plate dyed with ammoniacal eosin, the action, although still greatest in the blue and about the same in the violet, extends right up to the yellow-green, falling away rapidly, however, at this point. Ammoniacal erythrosin renders the action comparatively uniform from the green-blue to the end of the visible violet. In the green-blue there is a rapid falling-off, as is the case with eosin, followed by a rise in the green, the maximum action being reached in the yellow instead of the yellow-green as with eosin, and the action extends with lessening effect right through the orange. Ammoniacal rose Bengal gives a very similar effect, but the maximum is in the yellow-orange and extends further into the red. Ammoniacal cyanin has its maximum effect in the red.

Speaking generally, rose Bengal is the best sen-

sitizer for the yellow-green, and cyanin for the red. A solution of one part of the dye in ten thousand of water is a convenient strength to use, one part of ammonia being added to each hundred parts of water or alcohol. After soaking the plates for two minutes in the solution of the dye, they are washed to remove the excess of dye, and dried before exposure. As a rule, orthochromatic plates lose their sensitiveness and go wrong more rapidly than ordinary plates, and should be used as soon as possible after manufacture. They tend also to fog if forced in development. These drawbacks, however, are, as a rule, insignificant compared with the advantages gained in colour correctness, and it is only under trying conditions, such as long storage, that these defects interfere seriously with the use of the plates. The brands of colour-sensitized plates now in the market have reached great perfection and possess better keeping properties than the early orthochromatic plates.

Cœrulein, alizarin blue, and other dyes are used as sensitizers for the red, besides those mentioned.

CHAPTER XII.

IMPURITIES AND SUBSTANCES THAT ALTER IN THE AIR.

It is extremely probable that no substance has ever been obtained chemically pure. No one who has not occupied himself in chemical research, or read the memoirs of those who have done so, can have any idea of the almost insuperable difficulties to be encountered in obtaining a substance in a state of purity. In fact, the word "pure" as applied to chemicals is entirely comparative. It is impossible to obtain pure water, for instance, in glass vessels and in the air, as the water attacks and dissolves out the alkali from the glass on the one hand, and dissolves air on the other. Distillation in platinum vessels in a vacuum is the only method of obtaining water in the pure state, and then the purity is probably far from absolute. Consequently, "pure" in a chemical dealer's list means freedom from any gross impurity. For many purposes the "commercial" variety of chemical answers quite as well for photographic purposes as the "pure," but there are instances in which it is necessary to guard against some par-

ticular impurity, and these cases are indicated below.

Water, as ordinarily supplied from the tap or the well, is a very impure material. Apart from actual suspended matter, well or spring water contains varying quantities of carbonate and sulphate of lime and magnesia, phosphates, nitrates, chlorides—generally of sodium—and a certain quantity of ammonia. Surface water usually contains more ammonia, not much lime and magnesia, but a certain quantity of peaty matter. Rain water is fairly pure unless the roof from which it is collected is particularly dirty. Occasionally a water contains iron, and there are rarer impurities which need not be considered here. The worst impurity from a photographic point of view is chloride, which reacts with silver nitrate to form insoluble silver chloride; excess of lime or magnesia is often objectionable, particularly where oxalates are used, as insoluble oxalates of lime and magnesia are formed; iron is, of course, fatal, but does not often occur; peaty matter is objectionable, as it stains printing papers. All these impurities may be removed by distilling the water, rejecting the first pint that comes over, as it contains nearly all the ammonia. Boiling is sufficient to precipitate the carbonates of lime and magnesia, or temporary hardness; but the sulphates, or permanent hardness, still remain.

Commercial sulphuric acid contains lead and other impurities. Acid of good quality is so cheap

that it should be used for all photographic purposes. It should not be exposed to the air, as it absorbs water rapidly; and in diluting, the strong acid should always be added to the water instead of *vice versa*, as great heat is developed.

Commercial hydrochloric acid or muriatic acid invariably contains iron. Photographers should avoid an acid that shows any trace of yellow.

Alkalies, whether caustic or carbonate, contain various impurities. It is well to filter the solutions, when making up concentrated developers, etc., through a plug of asbestos or glass wool, or to allow the solution to stand and decant off the clear portion. Alkalies act strongly on the glass of the bottles containing them, and a clear solution generally has a deposit at the bottom after awhile. Alkalies should never be kept in stoppered bottles, as the stoppers become hopelessly fixed after a short time.

Cyanide of potassium deteriorates somewhat rapidly owing to the carbonic acid of the air turning out the prussic (hydrocyanic) acid. Old cyanide should never be used, as it probably contains nothing but carbonate. See that the cyanide you buy has not been in the shop for a long time!

Sulphocyanide is very hygroscopic—*i.e.*, it absorbs water from the air. For this reason it is best to convert it into, say, a 10% solution as soon as possible after purchasing.

Sulphites and bisulphites should be kept in stoppered or well-corked bottles, which should not

have a large air space above the crystals, as the air oxidizes them rapidly to sulphates, in which condition they are useless to the photographer.

Thiosulphate ("hypo.") as usually sold is pure enough for the photographer's purposes. When making up a solution, care should be taken to neutralize any acidity with a little ammonia or sodium bicarbonate. Thiosulphate solutions oxidize readily in the air, and fixing baths become acid on keeping. (See also p. 73.)

Ferrous sulphate contains more or less ferric salt, due to oxidation, and any crystals that show a yellow or brownish tinge should be picked out and thrown away. Some chemists keep pieces of metallic iron at the bottom of their solutions of ferrous sulphate, but a better plan is to fill a number of small bottles quite full, cork them, melt up some paraffin candle ends, and dip the tops of the bottles into the paraffin for a few moments. In this condition the contents of the bottles can be kept from the air until required. If the ferrous sulphate solution be put into a large bottle, air is admitted every time the stopper is taken out, and the air space above the solution gets larger as the material is used, so that deterioration goes on at an increasingly rapid pace.

Ferric chloride nearly always contains free hydrochloric acid, and sometimes ferrous chloride, but this is not usual. For etching purposes the presence of free hydrochloric acid is an advantage,

so long as there is not too much of it. Neutral or nearly neutral ferric chloride has a tendency to deposit basic salts—*i.e.*, compounds of oxide and chloride—and this should be guarded against. If too acid, the resist may come away from the plate when etching. Only experience can tell the etcher when his bath is in the right condition. If it shows a tendency to deposit, a little hydrochloric acid should be added; if too acid, it is well to add a little ferric hydrate, kept for the purpose and made by adding ammonia to ferric chloride solution, allowing the jelly to settle as far as it will, decanting off the clear portion, adding hot water, and again decanting.

Silver nitrate is generally pure, but does occasionally contain copper, which can be detected by the colour of the solution. It is necessary to keep all silver salts from the light, as they darken and spoil.

Gold chloride, as obtained commercially, contains hydrochloric acid, which requires to be neutralized with a little chalk or whitening. Instead of the pure salt, the double chlorides of gold with sodium or potassium are often sold. These are quite as convenient for photographic purposes as the pure chloride, and so long as the photographer gets his proper quantity of metallic gold, it is of no consequence whether it is in the form of pure chloride or not.

CHAPTER XIII.

RECOVERY OF RESIDUES.

THE waste gold, silver, and platinum salts contained in used up fixing- and toning-baths, spoilt sensitized paper, etc., are often saved and treated for the recovery of the metals. It is rarely worth the while of an amateur to trouble about saving his residues unless he works on a very large scale, but it is a matter that should not be neglected by the professional photographer. The fixing-baths, saturated with the double thiosulphate of silver and sodium, are most worth attention. Every five ounces of "hypo." is capable of taking up about two ounces of silver, and although the saturation point is never reached in ordinary practice, yet fixing-baths that have had a large number of plates and papers passed through them do contain a considerable proportion of silver. The old fixing-baths are thrown into a tub with a solution of "liver of sulphur"—a complicated mixture of sulphides and other things obtained by fusing sulphur with potassium carbonate—which precipitates the silver as sulphide. When the tub is nearly full, a sample should be taken in a test-tube or small vessel, and a few drops of liver of sulphur solution should be added to it. If no

precipitate forms, all the silver has been deposited; if the liquid turns brown, more liver of sulphur must be added to the tub. When the deposit has quite settled, the clear portion of the liquid should be drawn off through a tap in the side about a foot from the bottom. In time the sludge of silver sulphide will reach the level of the tap, when the cask should be emptied by running it out through a hole at the bottom, closed in the ordinary way by a wooden plug. Underneath the hole at the bottom of the cask, a large glass funnel containing a rag or filter should be placed, and the sludge should be run on to this: the liquid portion filters through, leaving the solid silver sulphide on the filter. It should be allowed to dry and then be labelled "silver sulphide," and sent to a refinery to be reduced.

Scraps of sensitized paper, gelatino-chloride, bromide, and other papers should be burnt to an ash, and forwarded to the refiner.

Toning-baths are treated with solution of ferrous sulphate, which reduces the gold to the metallic state.

The reduction of the silver is performed at the refiner's by fusing the sulphide, etc., with red lead, etc.; the resulting button of lead contains all the silver. The button is heated on a cupel or dish of bone-ash in a current of air. The lead is oxidized to litharge (PbO), which sinks into the cupel, leaving the silver behind.

CHAPTER XIV.

CELLULOSE.

CELLULOSE is the essential constituent of all the hard parts of plants, and its usefulness to mankind in general, and to the photographer in particular, is almost unlimited. Jute, hemp, paper, linen, cotton, etc., are all more or less pure forms of cellulose. Schleicher and Schull's filter-paper is pure cellulose, whilst cotton-wool and ordinary blotting-paper contain very little foreign matter. Pyroxylin, or gun cotton, is a nitrate of cellulose, and collodion is made by dissolving this in suitable solvents. Cellulose belongs to a large family, which, besides several closely allied forms of cellulose itself, includes starch, cane-sugar, grape-sugar, dextrin, and other bodies. They are all known in chemistry as carbo-hydrates, because they contain carbon and hydrogen and oxygen in the proportion to form water. Although their percentage composition has been known accurately enough for some time, the actual way in which they are built up is still being worked out, and although the materials out of which they are built

are so simple, the actual structure is very complicated. Cellulose, for example, is generally written ($C_6H_{10}O_5$) which means that chemists do not yet know how many $C_6H_{10}O_5$'s go to make up a complete molecule of cellulose. The same is true of starch and dextrin.

Cellulose is soluble in strong sulphuric acid, being converted into glucose or grape sugar, but if paper be passed through dilute sulphuric acid of specific gravity, 1.5, it is parchmented. Copper sulphate precipitated as hydrate of copper by ammonia solution, and dissolved in excess of the latter, forms the usual solvent for cellulose. Advantage is taken of this solubility in cuprammonia solution in the manufacture of "Willesden" paper. Thick paper is treated with the solution, which gelatinizes the surface, rendering it more resistant and waterproof. For roofing and similar purposes, two or three sheets of the paper are cemented together by the solution. Strong alkalies and zinc chloride disintegrate cellulose after a short time, but alkali of moderate strength, such as 15 per cent. solution of caustic soda, combines to form alkali-cellulose, adding considerably to the strength of the material.

This treatment with 15 per cent. alkali is known as "mercerizing." About seven years ago, Messrs Cross and Bevan discovered that if this mercerized cellulose be treated with carbon bisulphide, a soluble xanthate of cellulose is produced. This compound, which the inventors term "viscose," has

almost endless applications, many of which are of great interest to photographers, the important point about it being that from its solution in water, the cellulose can be recovered almost chemically pure. The solid "viscoid," made by coagulating viscose, closely resembles "celluloid" (see. below), and can replace it for many purposes, having the advantage of being practically unflammable.

By treating cotton-wool with nitric acid, various nitrates are formed. To secure good results it is necessary to have the nitric acid perfectly dry. As this is difficult to obtain in practice, a mixture of nitric and sulphuric acids is used, which produces the same effect as if perfectly dry nitric acid alone were employed. Three fluid ounces of nitric acid (sp. gr. 1429) are mixed with two fluid ounces of water in a large beaker-flask, and nine fluid ounces of strong sulphuric acid (sp. gr. 1839) are run into the mixture with constant shaking round. One hundred grains of dry cotton-wool divided into about ten pieces are dropped into the solution when its temperature has fallen to 150° F., and allowed to remain for 7 or 8 minutes, when the acid is drained off, the cotton being squeezed with a glass rod to squeeze out as much acid as possible. It is necessary to wash the cotton thoroughly to remove every trace of acid, when it may be dried in the air. This gun cotton, or pyroxylin as it is often called, is soluble in a mixture of alcohol and ether, but they must neither of them be methylated. The follow-

ing are convenient proportions for making plain collodion :—

Pyroxylin, . . .	1.2 grams, .	60 grains.
Alcohol (.820), . .	50 c.c., .	5 ozs.
Ether (.725), . . .	50 „, .	5 „

In winter it is convenient to use 5 c.c., or half an ounce more ether and the same quantity less alcohol. The formula for iodized collodion will be found on page 43.

Celluloid is a mixture of tri-nitro cellulose with camphor, and xylonite is a somewhat similar material. Other substances are added to reduce the inflammability of the first-named materials.

Paper can be tested for acid by pulping a convenient amount in a beaker-flask with a little boiling water, and adding one drop of alcoholic solution of methyl orange. If it turns red, acid is present. A dilute solution of iodine in potassium iodide is used as a test for "hypo." The amount of loading is ascertained by burning a given quantity of the paper to an ash and comparing with an equal weight of good filter-paper, treated in a similar manner.

CHAPTER XV.

RESINS, VARNISHES, ETC.

THE resins form a large class of complicated organic substances, found principally as exudations from trees in nearly all parts of the world. They are soluble as a rule in alcohol, ether, and benzene, but are insoluble in water. Photographers use them in making varnishes and in laying a dust ground in photogravure. The resins of most importance in this connection are colophony or common resin, lac, mastic, dammar, sandarac, dragon's blood, anime, copal, amber, caoutchouc, and gutta-percha.

Colophony varies in colour from pale yellow to dark red-brown, and is soluble in nearly all organic solvents and in hot linseed oil. Heated with caustic soda or potash it forms a resinate, which is an important constituent of yellow soap. Specific gravity, 1.07.

Lac resin owes its red colour to the insects whose bite causes the resin to exude from the tree. The most convenient variety to use is "shellac."

The specific gravity of the resin is about 1.12, and it is soluble in all the usual solvents, and in dilute hydrochloric and acetic acids, and in caustic alkalies. By treatment with chlorine, bleached lac is made. After bleaching, it should be kept under water, being dried shortly before use, as exposure to the air soon renders it insoluble. The freshly bleached lac forms a nearly colourless solution in alcohol, and is soluble in a hot solution of borax and in sodium carbonate. In a mixture of the last two solvents, it forms a water varnish, sometimes used for negatives, etc. An excellent waterproof ink can be made by rubbing up Indian ink with a solution of lac in borax (water, 1 oz.; borax, 130 grains; freshly bleached lac, 100 grains; sodium carbonate, 6 grains). Ordinary alcohol contains at least 5 per cent. of water, and as the alcohol evaporates in the cold faster than the water, the latter is left behind, dulling the surface of the lac. If heat be applied, however, the alcohol and water are driven off together, leaving a bright surface. This difficulty is not met with if the lac or other resin be dissolved in chloroform or benzene, which can be used cold.

Mastic occurs in pale yellow, transparent "tears," is brittle and sweet-smelling, melting at about 226° F. Alcohol or warm acetone dissolves it freely, and it is partly soluble in hot linseed oil, precipitating slightly on cooling. Specific gravity, 1.07.

Sandarac somewhat resembles mastic. It has a

specific gravity of 1.04, and dissolves readily in the usual solvents, including hot linseed oil.

Dragon's blood.—It dissolves in most of the usual solvents and in caustic soda and glacial acetic acid, but is insoluble in petroleum ether (benzine or benzoline), and but sparingly in ether or oil of turpentine. There is a good deal of variation, however, in its constitution and properties. It melts at about 250° F., and has a specific gravity of 1.197. In photography it is used as a resist when etching metal.

Elemi contains a large proportion (12½ per cent.) of volatile oil, is pale yellow in colour, and of various origin. It is very fusible, and is used to give toughness to lacquers and varnishes. Elemi is often adulterated, or a factitious product, consisting of colophony, Canada balsam, and essential oils, is substituted for it. The fraud may be detected by heating, when, after a short time, the turpentiney smell of the common resin is unmistakable.

Dammar is not very soluble in alcohol, more so in ether, and completely so in oil of turpentine, petroleum ether, etc.; it dissolves also in hot or cold solutions of sodium carbonate. Its specific gravity is about 1.05. Kauri gum is another form of dammara resin.

Anime and copal are obtained from various sources, some of them fossil, the latter being highly prized. Hard copal is light-brown in colour and makes excellent varnish. Its specific gravity is

generally between 1·06 and 1·07. Before being heated, copal is insoluble in alcohol, and only slightly soluble in ether or oil of turpentine. On heating, however, gases are given off, and the residue dissolves readily in ether and oil of turpentine.

Amber is insoluble in alcohol, essential oils, and in acids, with the exception of sulphuric acid. The specific gravity of amber varies from 1·05 to 1·10, and its melting-point is 550° F. Like copal, it is changed by heat, and is then soluble in alcohol and turpentine oil.

The balsams are resins containing varying proportions of essential oils and similar substances. Among these oleo-resins, Canada balsam is of importance to photographers. It is a pale yellow, transparent material, which forms a beautifully clear, glassy varnish. Canada balsam dissolves in benzol or chloroform, and is much used in this state as a medium for mounting microscopic objects.

Caoutchouc, or india-rubber and gutta-percha, are often confused, but they are quite different substances. Caoutchouc is a complicated body containing several different chemical substances, and varies a good deal in its properties according to its place of origin. It is soluble in coal-tar naphtha, ether, chloroform, bisulphide of carbon, benzene, and oil of turpentine. Its principal use in photography, besides india-rubber tubing, vulcanite dishes, etc., is for safe edging plates. Sulphur combines with caoutchouc, the product—vulcanite—being insoluble in any solvent,

not affected by heat or cold, much more elastic than caoutchouc, and generally more permanent.

As this is a somewhat miscellaneous chapter, it is convenient here to say a few words about oils and solvents. Oils may be divided into mineral oils, fixed oils, and essential oils. Essential oils nearly all possess the formula $C_{10}H_{16}$; they are very volatile and possess strong odours, which are sometimes due, however, to the presence of other volatile materials, such as cinnamic aldehyde in oil of cassia, benzoic aldehyde in oil of almonds, etc. Oils of turpentine, lavender, cloves, peppermint, etc., are examples of essential oils. They possess strong solvent powers, especially on resins.

The fixed oils are of vegetable and animal origin, and consist principally of mixtures in varying proportions of oleic, palmitic, stearic, and similar acids combined with glycerin. Alkalies combine with the acids, setting free the glycerin, and this is what happens when soap is made, soap being oleate, palmitate, stearate, etc., of soda or potash.

The drying oils contain linolic and linoleic acids, which are acted upon rapidly by oxygen if exposed to the air, a skin being formed which acts as an excellent waterproof varnish. Advantage of this property of drying oils is taken in mixing paints; it is not the colouring matter of the paint but the drying oil that affords the protecting surface. Lead salts assist this drying action, and a white or red lead paint dries very rapidly and forms an

excellent protection against weather. The principal drying oil is linseed; the following oils, however, possess drying properties to a less extent: hemp, walnut, poppy, and sunflower.

Castile soap should be made from pure olive oil. Once upon a time Marseilles soap was made from olive oil, and some of it may be still, but the greater portion of the Marseilles soap in the market is made from all kinds of oils.

Beeswax is the principal wax employed, but it is adulterated with paraffin, Carnauba wax, and Japan wax. Paraffin is used largely as an adulterant, and may be detected by treating the wax with oil of turpentine, which dissolves the beeswax and leaves the paraffin.

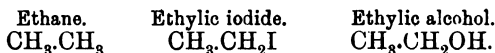
As regards solvents, two of importance are frequently confused: *benzene* and *benzine* are quite different bodies. The latter is light petroleum oil, sometimes called petroleum ether, whilst the former is the active constituent of coal-tar naphtha. Crude paraffin or petroleum oil contains a whole series of bodies known as paraffins, the lowest of which are gases—marsh gas (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10})—then come volatile liquids, beginning with pentane (C_5H_{12}), each member of the paraffin series differing from the next by CH_2 , then the burning oils, then the heavy oils—solar distillates, used for enriching water gas—then the vaselines, then the lubricating oils, and at last solid paraffins or paraffin wax. Benzine or benzoline

consists of the paraffins following and including pentane; all the liquid paraffins, however, possess strong solvent powers for grease, resins, and many other substances.

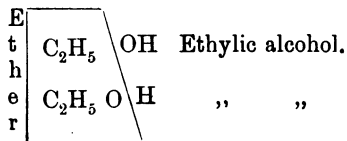
Benzene is obtained by refining light coal-tar oil, and is perhaps the most important compound known to chemists. It contains six atoms of hydrogen united to six atoms of carbon, and acts in all its properties and derivatives as if it were joined into a six-sided ring, as shown on page 57. It is sometimes called benzole.

Chloroform may be considered as marsh gas (CH_4) in which 3 H's have been replaced by 3 Cl's, its formula being CHCl_3 . It possesses great solvent powers, especially for fats.

By alcohol is meant ethyl alcohol. The alcohols form a series in the same way as do the paraffins, being derivatives of the paraffins. For example, ethane, by a round-about chemical process, can be converted into ethylic alcohol, thus:



From ethylic alcohol, ethylic ether or "ether" can be obtained by removing a molecule of water with sulphuric acid,



By oxidation, alcohol is converted into aldehyde (CH_3COH), and by further oxidation into acetic acid (CH_3COOH).

From acetic acid another solvent, acetone (CH_3COCH_3) is obtained. It is a powerful solvent of most organic substances.

Methylated spirit has crude wood spirit added to it for the purpose of making it undrinkable, so that the material, as sold, contains ethylic and methylic alcohols, besides acetone and various resinous materials.

It is interesting to note that pure methylic alcohol is the lowest of the series, being based on marsh gas (CH_4) in the same way that ethylic alcohol is based on the next member of the series, ethane. By similar treatment to that given above, methylic alcohol, methylic aldehyde, or formic aldehyde as it is usually called, and formic acid are obtained.

Carbon bisulphide is a compound of carbon and sulphur (CS_2). It is used principally as a solvent for india-rubber.

The following are useful formulæ for varnishes :—

Amber Varnish (Abney).

Fused amber (powdered),	.	.	.	1 part.
Chloroform,	.	.	.	16 parts.

May be used cold for plates or prints.

Collodion Varnish (Gamble).

Pyroxylin,	2 grams, 100 grains.
Ether (methylated),	50 c.c., . . . 5 ozs.
Alcohol (methylated),	50 „ . . . 5 „
Castor oil,	0.3 „ . . . 16 minims.

Varnish for Collodion Lantern Plates (Photogram).

Dammar,	1 part.
Benzole,	20 parts.

This varnish can be used cold.

Lac Varnish (Cooley).

Seed Lac or Shellac,	4 parts.
Rectified spirit,	20 „

Clear Mastic Varnish (Photogram).

Mastic,	14 ozs.
Canada balsam,	2 „
Sandarac,	6 „
Oil of turpentine,	44 „

Shake, and stand till clear; filter.

The mastic, sandarac, and turpentine oil must be dry. The longer it is left before use the better.

Gold-Coloured Lac Varnish (Cooley).

Ground turmeric,	$\frac{1}{2}$ lb.
Rectified spirit,	1 gall.

Macerate for a week, strain, and squeeze off, and add—

Gamboge,	$\frac{3}{4}$ oz.
Pale shellac,	6 ozs.
Sandarac,	1 $\frac{3}{4}$ lbs.

When dissolved, strain, and add further of turpentine mastic varnish (last formula), 1 pint.

This varnish is suitable for picture frames, brass and other metal work. The colour can be altered as desired by varying the constituents. By substituting dragon's blood for gamboge, a deep gold-coloured varnish is obtained. It is a good plan to keep the colouring matters separate in concentrated solutions, and add them as required.

By using annotta instead of turmeric, and dragon's blood instead of gamboge, a red varnish, suitable for wood, is obtained.

Ordinary Spirit Varnishes (Thorpe).

I. Brown hard—

Sandarac,	.	.	.	.	.	3 lbs.
Pale shellac,	.	.	.	.	.	2 „
Methylated spirit,	.	.	.	.	.	2 galls.

Dissolve and add 1 quart turpentine mastic varnish. Agitate well, strain through gauze, and after one month decant off clear portion.

II. White hard—

Sandarac,	.	.	.	.	.	5 lbs.
Camphor,	.	.	.	.	.	2 ozs.
Pounded glass,	.	.	.	.	.	3 lbs.
Methylated spirit,	.	.	.	.	.	7 quarts.

Dissolve, and, when strained, add 1 quart pale Canada balsam.

All the above are "spirit" varnishes. An "oil varnish" contains a drying oil in addition to the

resin and other constituents. The following is a good oil varnish suitable for wood-work, etc.—

Pale hard copal, 2 lbs.

Fuse and add—

Hot boiled linseed oil, 1 pint.

Boil until stringy, and thin with about 3 pints oil of turpentine.

CYCLOPÆDIC INDEX.

s. means soluble. | i. means insoluble. | dec. means decomposed.
 vs. " very soluble. | ss. " slightly soluble. | m. " mixes in all proportions,

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Acetone .	77, 137	Vinegar if dilute state	CH_3COCH_3	58	vs.	vs.	vs.
Acid, Acetic	137	Boric acid	$\text{H}_2\text{C}_2\text{H}_3\text{O}_2$	60	vs.	vs.	vs.
Boracic		Phenol .	H_3BO_3	62	.	.	.
Carbonic	33	.	H_2CO_3	62	vs.	.	.
Carbolic	56	.	$\text{C}_6\text{H}_6\text{O}$	94	vs.	vs.	vs.
Chromic	.	.	CrO_3	100	160	vs.	s.
Citric .	.	.	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + 2\text{H}_2\text{O}$	192	133	200	67
Formic	.	.	H.CHO_2	46	vs.	vs.	vs.
Gallic .	.	.	$\text{H}_3\text{C}_7\text{H}_5\text{O}_6 + \text{H}_2\text{O}$	170	s.	30	.
Hydrobromic	.	Muriatic acid,	HBr	81	.	.	.
Hydrochloric	19, 29, 120	spirits of salt	HCl	36.5	.	.	.
Hydriodic	.	.	HI	127.5	.	.	.
Hypo sulphurous	31	See Hydrochloric.	H_2SO_2	66	.	.	.
Muriatic	120	.	.	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Ammonium bichromate			$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	253	9	422	vs.
Bromide	44		NH_4Br	98	78	vs.	3
Carbonate		Sesqui carbonate	$(\text{NH}_4)_2\text{H}(\text{CO}_3)_2$	175	25	dec.	dec.
Chloride	32, 45	Sal-ammoniac	NH_4Cl	52.5	35	73	12
Fluoride			NH_4F	37	vs.	vs.	ss.
Hydrate	32	Ammonia (which see)	NH_4OH	35			
Iodide	44		NH_4I	145	165	vs.	25
Nitrate			NH_4NO_3	80	200	vs.	43
Oxalate			$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$	143	33	vs.	i.
Persulphate	84		$\text{NH}_4\text{S}_2\text{O}_8$	51	s.	s.	s.
Sulphide			NH_4HS	76	105	vs.	s.
Sulpho-cyanide	96, 97, 120	Ammonium thiocyanate	$(\text{NH}_4)\text{CNS}$				
Amidol	68, 69	Di-amido-phenol	$\text{C}_6\text{H}_3(\text{NH}_2)_2\text{OH}$	124	42		
Anime	132	Animi					
Artigue paper	112						
Asbestos	107, 120						
Asphaltum	114	Bitumen of Judea					
Atoms	15						
B							
Backing plates	81						
Balsams.	132						

Barium bromide	.	.	.	BaBr ₂ + 2H ₂ O	333	130	200	i.
Chloride	.	.	.	BaCl ₂ + 2H ₂ O	244	40	69	ss.
Iodide	.	.	.	BaI ₂ + 2H ₂ O	427	vs.	vs.	vs.
Hydrate	.	.	.	Ba(HO) ₂ + 8H ₂ O	315	.	dec.	i.
Peroxide	.	.	.	BaO ₂	169	i.	i.	i.
Benzene	56, 135	.	.	C ₆ H ₆	78	i.	i.	.
Benzine	135	.	.	.	.	.	.	.
Beaker flask	22	.	.	.	.	.	.	.
Bicarbonate of potash	.	.	.	.	.	.	.	.
of soda	.	.	.	.	.	.	.	.
Bichloride of mercury	.	.	.	.	.	.	.	.
Bichromate	.	.	.	Br	80	3.33	.	s.
Bromine	17, 22, 44	.	.	.	.	.	.	.
Br-mide paper	99, 100	.	.	.	.	.	.	.
Bromide	130	.	.	.	.	.	.	.
Borax	7, 8	.	.	.	.	.	.	.
Burette	94	.	.	.	.	.	.	.
Burton, W. K.	.	.	.	.	.	.	.	.
C								
Cadmium bromide	40, 44	.	.	CdBr ₂ + 4H ₂ O	344	1.06	vs.	30
Chloride	45	.	.	CdCl ₂ + 2H ₂ O	219	160	178	ss.
Iodide	40, 44	.	.	CdI ₂	366	90	133	102
Caoutchouc	133	.	.	.	.	.	.	.
Calcium bromide	.	.	.	.	.	.	.	.
Carbonate	119	.	.	CaBr ₂	200	140	312	s.
	.	.	.	CaCO ₃	100	i.	i.	i.
Chloride	107	.	.	CaCl ₂ + 6H ₂ O	219	132	228	13
Hydrate	.	.	.	Ca(HO) ₂	74	0.137	0.075	.
	.	.	.	Slaked lime	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Calcium hypochlorite .	.	Chloride of lime, Bleaching powder	CaCl_2OCl	127	ss.	.	.
Iodide .	.	Quick lime	CaI_2	294	200	450	s.
Oxide .	.	.	CaO	56	.	.	i.
Canada balsam .	132	.	.	.	.	.	.
Caramel .	81	See Mercurous chloride.	.	.	.	.	.
Calomel .	.	Charcoal, etc.	C	12	.	.	.
Carbon .	17, 33	See Ammonium carb.	CS_2	44	i.	i.	i.
Process .	104	See Potassium carb.	.	.	.	.	.
Bisulphide .	135	See Sodium carb.	.	.	.	.	.
Carbonate of ammonia	.	See Potass. hydrate.	.	.	.	.	.
of potash .	60	See Sodium hydrate.	.	.	.	.	.
of soda .	30, 60	.	.	.	.	.	.
Catechu .	108	.	.	.	.	.	.
Caustic potash .	32	.	.	.	.	.	.
Soda .	18, 32	.	.	.	.	.	.
Cellulose .	125	.	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$	.	.	.	.
Celluloid .	128	See Calcium carbonate.	.	.	.	.	.
Chalk .	.	See Calcium hypochlorite.	.	.	.	.	.
Chemical shorthand	18, 19	.	.	.	.	.	.
Chloride of lime	.	.	.	.	.	.	.

Chlorine .	17, 19	See Alum, chrome.	Cl	35.5	40	s.	.
Chrome Alum .	52			52.5	.	.	.
Chromium .	136		Cr	119.5	.	.	.
Chloroform .	33		CHCl_3	63	.	.	.
Copper .	.	Verdigris	Cu	200	7	20	7
Acetate .	.		$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$	2.23	vs.	vs.	s.
Bromide .	.		CuBr_2	170	60	vs.	s.
Chloride .	126	Blue stone, blue vitriol	$\text{CuCl}_2 + 2\text{H}_2\text{O}$	249	39	203	1.
Sulphate .			$\text{CuSO}_4 + 5\text{H}_2\text{O}$	245	60	dec.	i.
" Ammonio .	17	" Gas "	$\text{CuSO}_4\text{NH}_3 + \text{H}_2\text{O}$	.	.	.	.
Coal gas .	48			.	.	.	.
Coating dry plate	41			.	.	.	.
Wet plate .	117			.	.	.	.
Cerulein .	39, 40, 43,			.	.	.	.
Collodion .	46, 128			.	.	.	.
Dry plate .	49			.	.	.	.
Wet plate .	39, 40, 43, 46,			.	.	.	.
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Collotype .	113			.	.	.	.
Colophony .	129			.	.	.	.
Colour-sensitizers	116			.	.	.	.
Combined fixing and toning bath	97			.	.	.	.
Combining proportions	28			.	.	.	.
Copal .	132			.	.	.	.
Couple (electrical)	35			.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molec- ular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Crystalloids . . .	114	.	.	.	.	.	.
Cuprammonia solution . . .	126	.	.	.	.	.	.
Cyanin . . .	116	.	.	.	.	.	.
Corrosive sublimate . . .	.	See Mercuric chloride.	.	.	.	.	.
D							
Daguerre . . .	37	.	.	.	.	.	.
Daguerreotype . . .	38	.	.	.	.	.	.
Dammar . . .	131	.	.	.	.	.	.
Varnish . . .	136	.	.	.	.	.	.
Decantation . . .	23	.	.	.	.	.	.
Developing bromide prints . . .	100	.	.	.	.	.	.
Platinum . . .	107	.	.	.	.	.	.
Printing-out paper . . .	98	.	.	.	.	.	.
Development . . .	37, 38, 39	.	.	.	.	.	.
Developers :—							
Acetone . . .	76	.	.	.	.	.	.
Amidol . . .	68, 69	.	.	.	.	.	.
Eikonogen . . .	67	.	.	.	.	.	.
Ferrous oxalate . . .	54	.	.	.	.	.	.
Sulphate . . .	45	.	.	.	.	.	.
Glycin . . .	70	.	.	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
F							
Farnier, Howard	83			216.5	160	vs.	vs.
Ferric chloride . . .	27, 121	Chloride of iron, perchloride of iron	$\text{FeCl}_3 + 3\text{H}_2\text{O}$				
Hydrate . . .	26, 27		Fe(OH)_3	107	i.	i.	i.
Ferrous chloride . . .	29		$\text{FeCl}_2 + 4\text{H}_2\text{O}$	199	140	vs.	s.
Hydrate . . .	26, 27		Fe(OH)_2	90	i.	i.	i.
Oxalate . . .			$\text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}$	180	0.05	0.03	i.
Oxide . . .	25		FeO	72	i.	i.	i.
Sulphate . . .	25		$\text{FeSO}_4 + 7\text{H}_2\text{O}$	278	73	330	i.
Fish glue . . .	113						
Fixing . . .	77						
Fixing baths :—							
Wet plate . . .	46						
Dry plate . . .	77						
G							
Gamble, C. W.	87						
Gelatin . . .	46, 47, 113						
Tanning of . . .	75						
Gelatin-bromide emulsion . . .	50, 51						
Gelatin-chloride paper . . .	94						
Glass wool . . .	120						

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Bolling Water.	Cold Alcohol.
Hyposulphite of soda .	.	<i>See</i> Sodium thio-sulphate.	.	.	.	.	.
Hypochlorites .	84	.	.	.	.	.	.
I, J							
Impurities .	119	.	.	.	.	.	.
Intensification .	84	.	.	.	.	.	.
India-rubber .	41, 133	.	.	.	.	.	.
Iodine .	17	.	I	126.5	.	.	s.
Iodide .	22	.	.	.	.	.	.
Iron .	16	.	Fe	56	.	.	.
Perchloride .	27, 121	<i>See</i> Ferric chloride.	.	.	.	.	.
Printing in Salts of .	102	.	.	.	.	.	.
Isinglass .	113	.	.	.	.	.	.
Jones, Chapman .	84	.	.	.	.	.	.
K							
Kauri gum .	132	.	.	.	.	.	.
L							
Lac resin .	129	.	.	.	.	.	.
Dye .	130	.	.	.	.	.	.
Latent image .	39, 46, 48	.	.	.	.	.	.
Lea, Carey .	88	.	.	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
O							
Oils, drying	134	.	.	.	.	.	.
Essential	133	.	.	.	.	.	.
Fixed	133, 134	.	.	.	.	.	.
Mineral	133	.	.	.	.	.	.
Orthochromatism	115	.	.	.	.	.	.
Oxides	25	.	.	.	.	.	.
Oxidizing agents	27, 28	.	.	.	.	.	.
Oxygen	16, 17	.	O	16	.	.	.
Traps.	65	.	.	.	.	.	.
P							
Paper	128	.	.	.	.	.	.
Willerden	126	.	.	.	.	.	.
Palladium salts	105	.	.	.	.	.	.
Paramido-phenol	65	Rodinal	$C_6H_4.NH_2.OH$	109	1.2.	s.	4.5
Per cent. solutions	10	.	.	.	.	.	.
Petroleum ether	135	.	.	.	s.	s.	s.
Phenol	56	Carbolic acid	$C_6H_5.OH$	94	s.	s.	s.
Pipette	7	.	.	.	.	.	.
Pizzighelli, Capt.	104, 106	.	.	.	.	.	.
Paper	40	.	.	.	.	.	.
Poitevin's expt.	40	.	.	.	.	.	.
Positives on glass	41	.	.	.	.	.	.

Potassium	17	.	.	.	K	39	dec.	dec.	dec.
Bichromate	109	.	.	.	$K_2Cr_2O_7$	294	62	79	dec.
Bromide	22, 44	.	.	.	KBr	119	62	102	0.5
Carbonate	60	.	.	Pearl ash	K_2CO_3	138	110	156	i.
Chloride	45	.	.	.	KCl	74	33	57	.
Chloroplatinite	105, 106	.	.	.	K_2PtCl_6	488	0.93	5.3	.
Chromate	109	.	.	.	K_2CrO_4	194	10	94	i.
Cyanide	24, 77, 85, 120	.	.	.	KCN or KCy	65	s.	122	1.2
Ferricyanide	79, 83, 102	.	.	Red prussiate of potash	K_3FeCy_6	329	36	775	i.
Ferrocyanide	79, 102	.	.	Yellow prussiate of potash	$K_4FeCy_6 + 3H_2O$	422	26	50	i.
Hydrate	32	.	.	Caustic potash	KOH	56	200	vs.	vs.
Meta-bisulphite	58	.	.	.	$K_2S_2O_5$	222	33	.	i.
Printing-out-paper	94, 98	.	.	Gelatino-chloride or collodio-chloride	.	.	.	.	.
Precipitate	20	.	.	.	.	.	.	.	.
Purity	118	.	.	.	.	.	.	.	.
Pyrocatechin	57	.	.	Ortho-dioxy-benzene	$C_6H_4(OH)_2$	110	s.	s.	vs.
Pyrogallol	57, 61, 62	.	.	Pyrogallic acid (which see).	.	.	.	.	.
Pyro-stain	59, 74	.	.	.	.	.	.	.	.
R		.	.	.	.	.	.	.	.
Reducing agent	27, 28	.	.	.	.	.	.	.	.
Reduction	83	.	.	.	.	.	.	.	.
Residues, recovery of	123	.	.	.	.	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Resorcin .	57	Meta-dioxy-benzene	$C_6H_4(OH)_2$	110	vs.	vs.	vs.
Restrainer .	41, 56	.	.	.	.	.	.
Rodinal .	70	.	.	.	.	.	.
Rose Bengal .	116	.	.	.	.	.	.
Rubber solution	42	.	.	.	.	.	.
S							
Sandarac .	131	.	.	.	.	.	.
Schlippe's salt .	.	See Sodium sulph-antimoniate.	.	.	.	.	.
Sensitizing wet plates	42	.	.	.	.	.	.
Carbon tissue	109	.	.	.	.	.	.
Albumen paper	90	.	.	.	.	.	.
Sepia tone	105	.	.	.	.	.	.
Shellac .	130	.	.	.	.	.	.
Silver .	17	.	Ag	108	.	.	.
Albumenate	91	.	.	.	.	.	.
Bath .	41, 42	.	.	.	.	.	.
Bromide	22, 23, 41, 44	.	AgBr	188	i.	i.	i.
Chloride	21, 22, 23, 45	.	AgCl	143	i.	i.	i.
Cyanide	.	.	AgCN	134	i.	i.	i.

[illegible]

NAME.	Reference Pages.	Other Names.	Symbol.	Molecular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
Sodium thiosulphate	31, 46, 54, 77, 78, 121	Hyposulphite of soda, "Hypo."	$\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$	248	100	vs.	i
Solarisation	81	.	.	.	.	.	.
Solvents	135	.	.	.	.	.	.
Spectrum	115	.	.	.	.	.	.
Speed of plates	72	.	.	.	.	.	.
Stewing emulsion	51	.	.	.	.	.	.
Stock solutions	64	.	.	.	.	.	.
Sulphites, action of	58, 120	.	.	.	.	.	.
Sulphur	17, 133	Brimstone, flowers of sulphur	S	32	i.	i.	i.
Liver of	123	.	.	.	.	.	.
T							
Table — weights and measures	9, 10	.	.	.	.	.	.
Thermometer scales	12	.	.	.	.	.	.
Silver salts	23	.	.	.	.	.	.
Bromides	44	.	.	.	.	.	.
Iodides	44	.	.	.	.	.	.
Chlorides	45	.	.	.	.	.	.
Sodium carbonates	61	.	.	.	.	.	.
Gold toning baths	92	.	.	.	.	.	.
Tanning of gelatin	75	.	.	.	.	.	.

NAME.	Reference Pages.	Other Names.	Symbol.	Molec- ular Weight.	Solubility in 100 Parts of		
					Cold Water.	Boiling Water.	Cold Alcohol.
W							
Washing	14		.	.	.	.	.
Washing soda	17, 119	See Sodium car- bonate.					
Water	29		H ₂ O	18	.	.	.
Of crystallization	130		.	.	.	.	.
Waterproof ink	81		.	.	.	.	.
Waterhouse, Col. J.	41, 42, 43		.	.	.	.	.
Wet plate			.	.	.	.	.
Z							
Zinc	33		Zn	65	300	vs.	100
Chloride	128		ZnCl ₂	130	vs.	vs.	s.
Bromide	44		ZnBr ₂	225	320	vs.	s.
Iodide	44		ZnI ₂	319	vs.	vs.	s.

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